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Evaluation of a Trans-Portable Gas Chromatographic Mass Spectrometer

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for May 2017 to October 2019

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14. ABSTRACT

For all branches of the military, field-surveillance of toxic compounds is mission critical. To fulfill this requirement, equipment is needed that can provide sensitive and robust identification and quantification of volatile and semi-volatile organic compounds. The HAPSITE-ER (HER) is a human-portable gas chromatograph-mass spectrometer (GC-MS) currently employed by USAF for that purpose. It's current iteration was initially released in 2008. The work described herein is the evaluation of a newer, transportable GC-MS that has the potential to deliver laboratory performance from a fielded instrument.

Replacement of the HER would require equipment that is easily field deployable. Therefore it is critical that equipment is chosen that is rugged enough to be subjected to transport, maintains a stable calibration between uses, and is self-contained. The candidate instrument is Griffin 460/465 (hereafter: Griffin; FLIR Systems), a ruggedized transportable unit. The Griffin has many of the same features as the HER, which includes: continuous monitoring (probe); thermal desorption (TD); headspace; and SPME while also providing for direct liquid injection of samples as well as limited tandem mass-spectrometry.

This study evaluated the Griffin principally for TD applications. Despite the additional capabilities offered by the Griffin, flaws were observed in some of the more fundamental operations of this instrument that would preclude its use as a fielded instrument for the U.S. military. Specifically, our data suggests that the mass spectrum generated during analysis is of questionable fidelity and reproducibility while introduction of samples via TD functioned properly, at best, on a sporadic basis. Significant and numerous inquiries made to the manufacturer failed to provide resolution to the observed malfunctions.

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1.0 SUMMARY

The goal of this study was to compare the FLIR Griffin 460/465 (Griffin) to the HAPSITE-ER (HER). The units were compared for physical and operational characteristics. Previous work has extensively characterized the operational performance of the HER using an approach developed by us known as Focusing Agents[2] (FA). To make a relative comparison of the two instruments, similar experiments using FA were analyzed on a Griffin, yielding peculiar results. More specifically, the mass spectra generated by the Griffin lacked sufficient quality to generate a reliable positive identification of analyzed compounds. This result was reproduced via both direct liquid injection as well as TD. Additionally, sample introduction using TD yielded data of poor and inconsistent quality. The performance is discussed fully within this report.

2.0 INTRODUCTION

2.1 Rationale for Research

HER reliabilty has been a subject of discussion and was listed in U.S. Air Force Medical Service Gap 63 (ACC): Portable Chemical Screening Analysis. The Griffin was examined as a potential replacement for the HER under equipment modernization. Specific goals sought by replacement of the HER include improving data quality for quantitative analyses and introduction of novel instrument capabilities relative to the HER. As our laboratory has previously completed an extensive characterization of the HER TD capabilities with regards to quantitative analysis of CWA simulants we evaluated the Griffin units using a similar approach. This study not only evaluates and compares the HER and the Griffin based upon those criteria but also based upon physical and operational characteristics that are considered mission critical for field portable equipment. Figures 1 and 2 are photographs illustrating the units under investigation.

Figure 1. FLIR Griffin 460

Figure 2. Inficon HAPSITE-ER

3.0 METHODS

3.1 Equipment and Supplies

A Hazardous Air Pollutants On-Site Extended Range (HAPSITE-ER) GC-MS was purchased from Inficon (Syracuse, NY) containing a 15'DB-5 column (100% Polydimethylsiloxane column (15 m X 0.25 mm, 0.19 µm film thickness).

Both the Griffin®460 and Griffin®465 were purchased from FLIR® (West Layfayette, IN). The FLIR® X-Sorber, an option for collecting air samples with an embedded field pump that holds two thermal desorption tubes was an option purchased with the Griffin®460. The X-Sorber is required for analysis of TD tubes using the Griffin units. Both the Griffin 460/465 contained a 15 m DB-5 column.

The following chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA): diethyl malonate (Sigma Item#04151-1mL), diethyl malonate-2-$^{13}C_2$ (Sigma Item#281859-1G), diethyl malonate-1,3-$^{13}C_2$ (Sigma Item#488798-250mg), and diethyl malonate-1,2,3-$^{13}C_3$ (Sigma Item#488771-250mg). Optima™ LC/MS Grade Methanol was purchased from Fisher Chemical

(Item#A456-4; Waltham, Massachusetts, USA). TD tubes were purchased from Supelco (Bellafonte, PA, USA) are stainless steel (3.5” x 0.25”) and contain Tenax™ TA of 35/30 mesh. HER used TD tubes with the same packing but constructed of glass.

3.2 TD Tube Preparation – Standards Prep

Stock solution preparation of diethyl malonate (DEM) and its isomers are shown in Table 1. The nomenclature used is for the primary fragment as established by the NIST mass spectral database. The isotopically unlabeld compound with is labelled as DEM_{115} and each additional isotope adds one mass unit ($DEM_{116-118}$).

Table 1. Preparation of stock solutions of DEM

Analyte	**Amount**	**Volume**	**Concentration**	**ID**
DEM$_{115}^{a}$	9.3 mg	1 mL	9,300 ng/µL	Lot#BCBO9716V
DEM$_{116}^{b}$	9.9 mg	1 mL	9,900 ng/µL	Lot#MBBC1142
ĐEM$_{117}^{c}$	21.1 mg	1 mL	21,100 ng/µL	Lot#MBBC2236
DEM$_{118}^{d}$	32.8 mg	1 mL	32,800 ng/µL	Lot#MBBB6433V

^{a}MW=160; ^{b}MW=161; ^{c}=MW=162; and ^{d}MW=163

Working Solution A~1:50 dilution from above stock solution into MeOH

Analyte	**Concentration**	**Aliquot**	**Volume**	**Concentration**
DEM$_{115}$	9,300 ng/µL	2.7 µL	5 mL	5.02 ng/µL
DEM$_{116}$	9,900 ng/µL	100 µL	5 mL	198 ng/µL
ĐEM$_{117}$	21,100 ng/µL	100 µL	5 mL	422 ng/µL
DEM$_{118}$	32,800 ng/µL	100 µL	5 mL	656 ng/µL

Working Solution B—1:40 dilution from Working Solution A into 5mL MeOH

Analyte	**Concentration**	**Aliquot**	**Volume**	**Concentration**
DEM$_{116}$	198 ng/µL	125 µL	5 mL	4.95 ng/µL
ĐEM$_{117}$	422 ng/µL	125 µL	5 mL	10.5 ng/µL
DEM$_{118}$	656 ng/µL	125 µL	5 mL	16.4 ng/µL

Working Solution C~1:40 dilution from Working Solution A into MeOH

Analyte	**Concentration**	**Aliquot**	**Volume**	**Concentration**
DEM$_{115}$	5.02 ng/µL	199.2 µL	1 mL	0.999 ng/µL
DEM$_{116}$	198 ng/µL	10.1 µL	5 mL	1.999 ng/µL
DEM$_{117}$	422 ng/µL	11.8 µL	5 mL	4.98 ng/µL
DEM$_{118}$	656 ng/µL	15.25 µL	5 mL	10.0 ng/µL

Aliquots of Working Solution B/C were injected onto the TD tubes using the Markes CSLR (depicted in Figure 3.)

Figure 3. Markes Internatinal CLSR

3.3 Parameters and Conditions of FLIR GCMS and HAPSITE-ER Analysis

The operating conditions for HER and Griffin were identical and were originally supplied from a CWA method from Inficon. However, the Griffin required a few minor changes in operating conditions are shown in Table 2.

Table 2. GC oven ramp program

Start	**Ramp Rate (ºC/Min)**	**Ramp Time (Min)**	**Temperature (ºC)**	**Hold Time (Min)**
00:00			40	02:00
31:00	10.0	24.00	280	05:00
35:00	05.0	4.00	300	00:00

Table 3 illustrates a comparison of the operating parameters between the MS units from both companies.

Table 3. GC column and flow parameters

	HAPSITE-ER	Griffin 460/465
Column Information	15 m, db-1MS, 0.25 mm i.d., 1.0 um df (standard)	Standard VB-5MS (15M x 0.18mm x .18µm); others available
Temperature Range (TDSS)	45-330	40-300
Column Temperature Range	40-200	40-300
In	N2	Front SS Inlet H2 (or He)
Out	Quadrapole MS	Ion Trap MS
Initial	45 ºC	40ºC
Pressure	NA	8.7465 psi
Flow	1.0 mL/min	1.5 mL/min
Average Velocity	NA	31.404 cm/sec
Split Ratio	No Split	22.1% (minimum)
Solvent Delay	1.00 min	1.13 min
Flow Setpoint		On
(Initial)	1.5 mL/min	

3.4 Physical Characteristics

Table 4 illustrates some key differences between HER and Griffin. HER is approximately ½ the weight and is considered portable. While Griffin is considered transportable. HER can run on battery power while Griffin requires line power. One advantage of Griffin is the ability to run off of hydrogen which can easily be supplied by a hydrogen generating unit.

Table 4. Comparison of Physical/Operating Conditions

		HAPSITE-ER		**FLIR 465**
Physical Characteristics				
L X W X H (inches)		18 X 17 X 7		19.2 X 19.2 X 21.1
Weight (lbs)		42 w/battery		99.5
Environmental Operating Temperature (°F)		41-113		41-104
Power (DC)		24V rechargeable NiMH battery (2-3 hr life)		NA (shore power only)
Power (AC)		AC converter		100-240VAC
Screen		6.5 VGA color display with touch screen		None
Mobility		Backpack available, can be carried by an individual		Vehicle mounted
Computer				
Hard Drive		16 Solid State Flash Drive		500GB
Data Analysis		AMDIS Mass Spectral Libraries, NIOSH, (NIST on optional laptop)		Griffin™ System Software (GSS); Griffin™Lib, NIST, and AMDIS mass
Communication		802.11G wireless or direct Ethernet connection		Ethernet connection TCP/IP
Gas Chromatograph				
Carrier Gas		Nitrogen		Connection for external gas source (choice of He or H2); gas available from many vendors; H_2 generator available
GC column		15 m, db-1MS, 0.25 mm i.d., 1.0 um df (standard)		Standard VB-5MS (15M x .18mm x .18µm); others available
Temperature range (°C)		45-200		40-300
Sample Introduction		Splitless only		Split/splitless
		NA		Direct syringe injection (1 syringe included)
		SPME fiber (optional)		SPME fiber (optional)
		Manual headspace sampler (optional)		Manual headspace sampler (optional)
		NA		Autosampler (optional)
		sampling line w/probe for real-time analysis		heated sampling line w/probe for real-time analysis (Griffin™ 465 model)
		NA		PSI-Probe™ thermal separation via TAG™ (optional)
		NA		PSI-Probe thermal separation via GERSTEL-Twister® (optional)
		SituProbe Purge and Trap for water analysis		Griffin™ Purge and Trap for water analysis (optional)
		Thermal Desorber Sampling System		Thermal Desorber Sampling System w/Griffin™ X-Sorber handheld vapor sampler (optional)

Table 4: Comparison of Physical/Operating Conditions (continued)				
		Mass Spectrometer		
Detector Type		Quadrupole		Ion Trap
Ionization Type		electron ionization (EI)		electron ionization (EI)
Mass range and scan rate		41-300 (1-300 using SIM) ; 1000 AMU/sec @ 10 points per AMU		35-425 m/z; up to 10,000 m/z per second @ 20 points per m/z
MS/MS-capable?		No		Yes
Detector		Electron Multiplier		Conversion dynode electron multiplier
Vacuum System		Non Evaporable Getter (NEG) Pump : optional service module		mini turbomolecular pump
Tuning Compound		Bromopentafluorobenzene (delivered through canister)		On-board FC-43 (Perfluorotributylamine)

3.5 Sample Preparation – Manual Injection Method

Using the standards deccribed in Section 3.2, the following amounts were used in the preparation of TD tubes for our experiments (Table 5).

Table 5. TD Tube Preparation

Injection Volume	**Multi-component solution (nanograms)**			
	115	116	117	118
1µL	0.999	1.999	4.98	10.0
2µL	1.998	3.998	9.96	20.0
4µL	3.996	7.996	19.92	40.0
	Individual Component Solution			
1 µL	0.999	1.999	4.98	10.0
	Individual Component Solution (~10X)			
1 µL	10	20.8	45.8	85.2

4.0 RESULTS

Analytical investigations were conducted on the Xsorber, which is a combination sampler and thermal desorption unit which interfaces with the Griffin. The purpose of these experiments was to compare the results to the work previously established with the HER. The HER work was published[1,2] and described significant improvement of field results when Focusing Agents (FA) are employed. These results demonstrated how intra-instrument and inter-instrument results were improved with HER. It was determined that FA could be used to also examine the reliability/stability of the Griffin.

Over the course of the experimentation, it was determined that the ion trap was not stable and generally did not yield the expected spectra and this is discussed in the following sections.

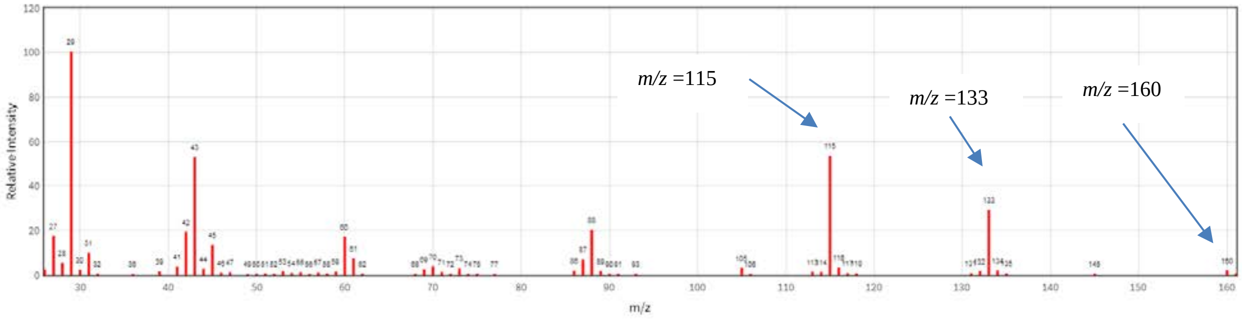
Additionally, the Griffin has several modes of analysis that were employed in our experiments: Direct Column Injection (DCI) and Thermal Desorption using their Xsorber™ (TDX) unit. Furthermore the TD port also provides a mechanism to by-pass TD transfer, this will be referred to as the TD Injection (TDI). Unfortunately, TDX was found to be unreliable (Section 4.1.3.1) and we used TDI (Section 4.1.3.2) to examine the path used by thermal desorption.

4.1 Generation of Mass Spectra

4.1.1 Comparison to NIST Database

Figure 4 (below) illustrates a typical mass spectrum of unlabeled DEM, the compound used as a model for the work to compare the HER and Griffin instruments. As described in the literature[2], the isotopic analogs of DEM were used as normalizing agents to account for run-to-run variability. Analysis of FA using the HER confirm that DEM fragmentation yields a mass spectrum comparable to the commercial NIST database (shown below).

Figure 4. NIST mass spectrum of unlabeled DEM

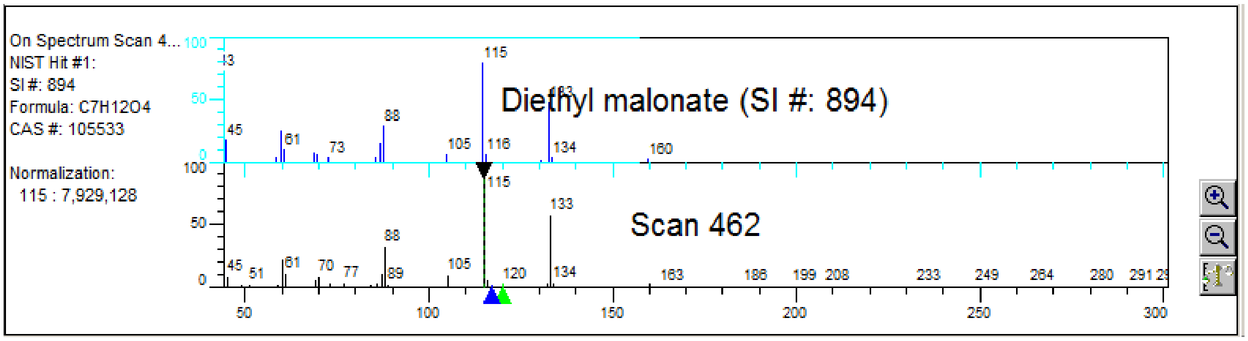


While the HER uses a qudrupole mass-selective (Q-MS) detector, the Griffin incorporates an ion trap mass selective (IT-MS) detector. Fitzgerald et al.[3] and Thermo Fisher[4] have demonstrated that the IT-MS should, in general, yield spectra that are comparable to that of the Q-MS. The ability to create mass spectra that are typical of those found in commercial databases is a critical function required for the assignment of tentative identifications for unknown compounds encountered in a sample. It is also a requirement for conducting quantitative measurements of samples utilizing a stable isotope labeled internal standard, a common laboratory practice. A typical spectrum from Griffin is illustrated in Section 4.1.3.

4.1.2 HAPSITE-ER

Mass spectra produced by the HER closely resemble the NIST spectra for DEM (Figure 5, top section).

Figure 5. HER Mass Spectrum of DEM compared to NIST reference library

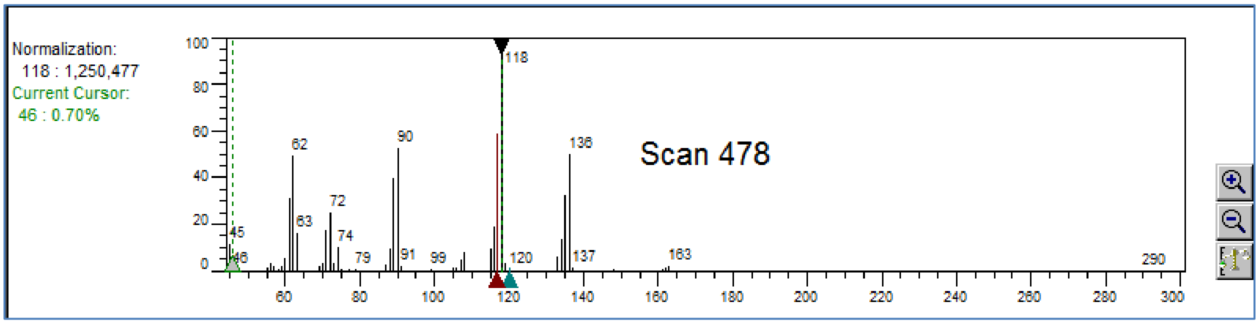


On Spectrum Scan 4...
NIST Hit #1:
SI #: 894
Formula: C7H12O4
CAS #: 105533

Normalization:
115 : 7,929,128

The HER mass spectrum of unlabeled DEM is illustrated in Figure 5 (bottom). When the four isotopic analogs are used, HER provides a mass spectrum with the correct ratio for all four base peaks at m/z=115-118 (Figure 6). The ratios are reflective of the concentrations (1:2:3:4 for $DEM_{115-119}$, respectively). Because the chemical properties of isotopic analogs are identical, it can be concluded *a priori* that equal amounts of each DEM analog will produce an equal response from the detector for each analog. Table 6 shows typical area response for the four isotopic analogs on HER. For comparison, the third column shows the area counts after normalization by the loaded mass. The normalized responses show consistency and agreement between the isotopic analogs' base peaks (RSD < 10%).

Figure 6. HAPSITE ER Mass Spectrum of DEM Multi-Component Mixture



Normalization:
118 : 1,250,477
Current Cursor:
46 : 0.70%

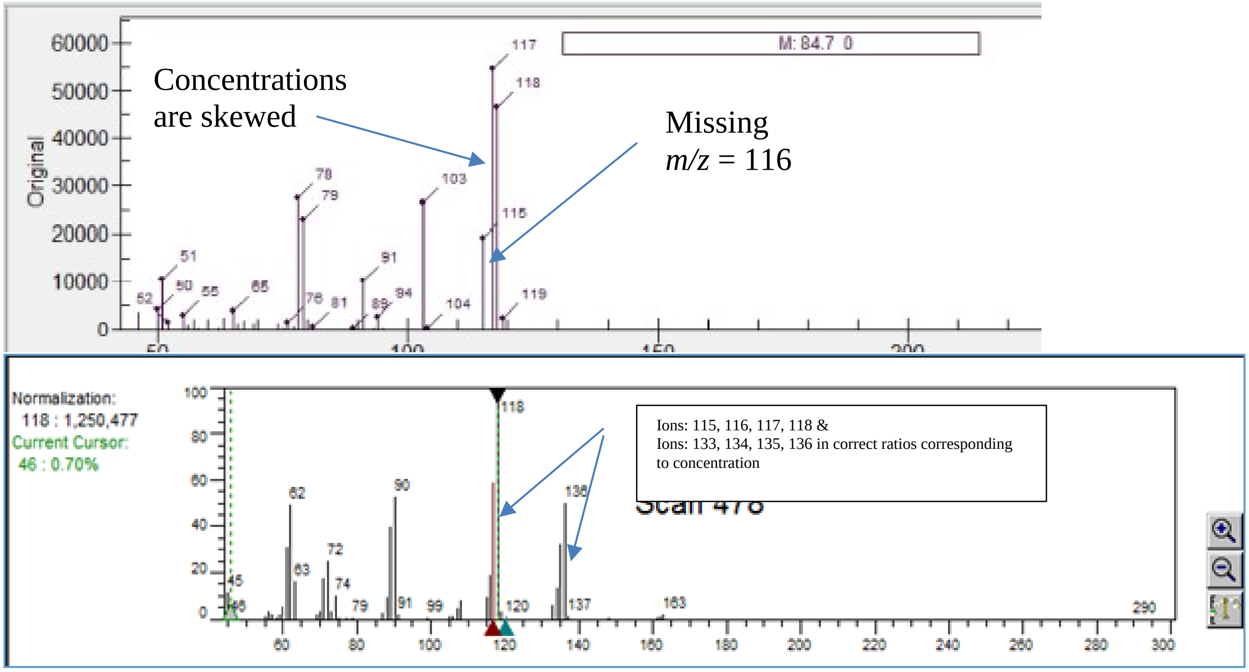
Table 6. Area response of Isotopic Mixture (HER)

Multi-Component Mixture	Area Count	Normalized by ng Loaded
DEM$_{115}$ @ 2 ng	1060400	530200
DEM$_{116}$ @ 4 ng	2168608	542152
DEM$_{117}$ @ 10 ng	5773194	577319
DEM$_{118}$ @ 20 ng	9394915	469746

4.1.3 Griffin

Mass spectra produced by the Griffin show marked deformation relative to the NIST database and the data produced by HER (Figure 7).

Figure 7. Griffin Mass Spectrum of DEM Multi-Component Mixture and the HAPSITE-ER mass spectrum of multi-component mixture of DEM isotopic analogs.



Concentrations are skewed

Missing *m/z* = 116

Ions: 115, 116, 117, 118 &
Ions: 133, 134, 135, 136 in correct ratios corresponding to concentration

Table 7. Area response of isotopic mixtures - Griffin

Concentration (ng)	20	41.6	91.6	170.4
	DEM$_{115}$	**DEM$_{116}$**	**DEM$_{117}$**	**DEM$_{118}$**
Direct Inject#1	216,967	1,216,000	3,547,000	5,802,000
Direct Inject#2	225,049	981,231	2,698,000	2,578,000
Direct Inject#3	181,622	867,603	3,186,000	5,433,000
Direct Inject#4	219,312	1,055,000	3,027,000	5,475,000
Direct Inject#5	193,347	1,105,000	3,160,000	5,214,000

Most evident is the complete absence of a peak at *m/z* 116. Additionally, the concentration differences between the four analogs should show a ladder-like increase from left to right on the mass spectrum (*m/z* 115-118), but instead show skewed abundances relative to the loaded amounts. When the data is normalized in a fashion similar to the analysis done on the HER data the RSD ranges from 40-48%.

4.1.3.1 Griffin Xsorber (TDX)

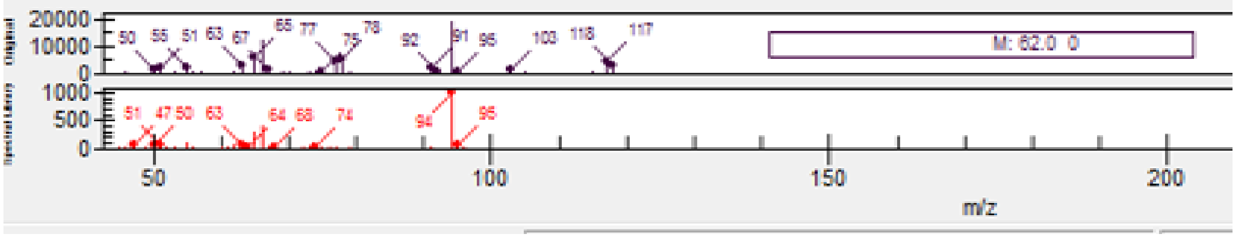
Unfortunately, full characterization of the Griffin (thermal desorption) could not be performed due to performance issues with the TDX. The TDX is a combined TD tube sampler that docks with the Griffin via a dedicated port that is independent of the direct inject port. This configuration allows the TDX to thermally desorb onto a cold trap/concentrator.

Table 8. Xsorber Results

Concentration (nanograms)	20	41.6	91.6	170.4
	m/z$_{115}$	**m/z$_{116}$**	**m/z$_{117}$**	**m/z$_{118}$**
TD #1	3,702	57	12,823	20,273
TD #2	6,425	81	23,430	17,592
TD #3	5,793	ND	24,462	20,370
TD #4	6,522	ND	17,386	20,657
TD #5	5,644	ND	21,814	20,257

Very little useable data was obtained using the TDX. However, one example is observed in Table 8 and Figure 8.

Figure 8. Xsorber Mass Spectrum of DEM multi-component mixture



The results using the Xsorber exhibited the loss of m/z=116 associated with DEM_{116} (MW=161). Further work was conducted by removing the Xsorber and injecting directly into the TDX port (TDI), as was described in consultations with FLIR.

4.1.3.2 TDX Port Direct Column Injection (DCI)

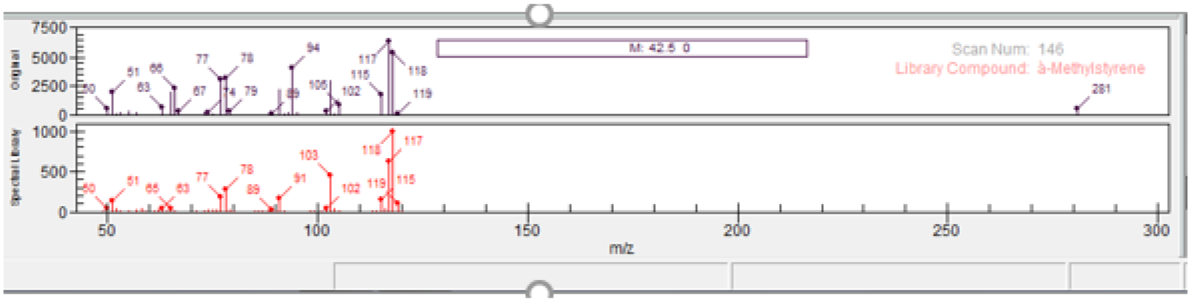
Further work to investigate the TD port was done by direct (liquid via syringe) column injection into the dedicated TDX port. Table 9 shows data generated by directly injecting each isotopic analog individually into the TDX port. Note that the "X" next to each result illustrates area that appears to be carry-over from previous analyses (less likely) or is an inappropriate mass assignment/determination by the Griffin. Based upon experience, we attribute these results to the performance of the ion trap detector. A typical result demonstrates the performance of the ion trap (Figures 7 & 8) and its inability to observe all the ions on a multi-component isotopic mixture.

Each isotope was injected separately resulting in interesting data. First, the ions associated with DEM_{161} should yield fragments at m/z=116. None are observed even with pure DEM_{161}. Furthermore, the area for DEM_{162} should be less than that of DEM_{163}. We were not able to resolve this with the TDX and observed this phenomenon with the TDI and DCI analyses.

Table 9. Single Isotope Injection via DCI

Single Component Injection	Concentration (nanograms)	m/z = 115	m/z = 116	m/z = 117	m/z = 118
DEM_{160}	1	97182	ND	315176 X	267809 X
DEM_{161}	2	120027 X	ND	374779 X	301747 X
DEM_{162}	5	93679 X	ND	286999	235056 X
DEM_{163}	10	81835 X	ND	254927 X	210473

Figure 9. TDX Griffin Mass Spectrum of DEM and Multi-component

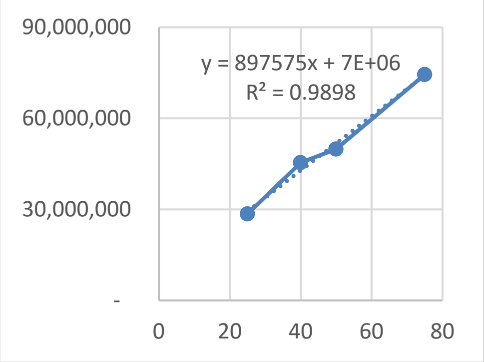


For comparison the same solution was analyzed on HER and the results are shown in Table 10 and Figure 10. The results demonstrate that the HER quadrupole yields linear results.

Table 10. DEM Multi-Component Injection on HER

Isotopic Analog	Concentration (nanograms)	Area
DEM_{116}	25	28,490,832
DEM_{115}	40	45,391,128
DEM_{117}	50	49,882,356
DEM_{118}	75	74,402,096

Figure 10. Linear regression of HER Multi-Component Injection



Additional work was conducted by injection directly onto the column which bypasses the Xsorber path. This is discussed in the next section.

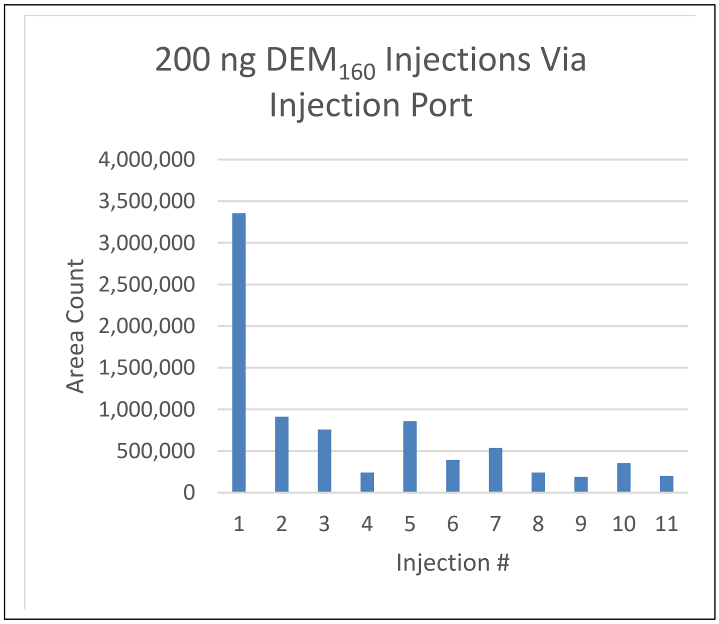
4.1.3.3 Griffin Direct Column Injection

DCI allows by-passing the thermal desorption path and using Griffin in a more conventional mode. This is a feature that Griffin has that is not present on HER. In Table 11 and Figure 11, we examined multiple injections of DEM$_{115}$. Note there were a few injections of varying isotopes that are not shown.

Table 11. DEM Reproducibilty on DCI

DEM$_{160}$		
Injection	Amount (nanograms)	Area
1	200	3,356,000
5	200	913,329
6	200	758,915
7	200	241,266
8	200	858,721
9	200	393,172
10	200	537,439
11	200	242,003
12	200	190,685
13	200	355,153
14	200	201,254

Figure 11. DEM Reproducibility



The data shows a steady decline in the area response. This performance was observed consistently with hydrogen as a carrier gas. Similar results when fragment m/z=133 was examined.

To determine the effect of hydrogen on the ion trap, we converted to helium as the carrier gas. No substantial improvement occurred and the results are further discussed in the next section.

4.2 Assessment of Griffin Performance

Multiple experiments initially conducted using the typical base-peak ions at *m/z* 115-118 (discussed above) illustrated inconsistency in the recoveries. Furthermore, the stable isotopes of diethyl malonate (DEM) resulted in surprising fragmentations. Consistently, signal from DEM$_{116}$ (MW 161, fragment = m/z 116) at 25 ng was extremely low or absent. The reconstructed ion chromatogram/mass spectrum for the Griffin is shown in Figure 7, this is compared to the expected result in Figures 5 and 6. Additional work could not determine the anomaly causing m/z 116 to disappear other than to suggest that it resulted from the ion trap. This anomaly was also observed with direct injection analyses.

Table 12. Multi-component Analysis – Injection By Direct Column Analysis (He Carrier Gas)

Concentration	20	41.6	91.6	**170.4**
	DEM_{115}	**DEM_{116}**	**DEM_{117}**	**DEM_{118}**
Direct Inject#1	216,967	1,216,000	3,547,000	5,802,000
Direct Inject#2	225,049	981,231	2,698,000	**2,578,000**
Direct Inject#3	181,622	867,603	3,186,000	5,433,000
Direct Inject#4	219,312	1,055,000	3,027,000	5,475,000
Direct Inject#5	193,347	1,105,000	3,160,000	5,214,000

The use of FA with Griffin data is illustrated in Table 12. Interestingly, the ions for each isotope were present (m/z = 115, 116, 117, 118). Additional work with He would have been interesting to pursue, but the instrument was intended to perform using hydrogen. Not enough work was performed to make a strong case. Nonetheless, the data is reported in Table 9.

The Relative Response Factor was calculated for DEM_{115} as follows:

$$RR_{\text{"fa,118, average"}} = \frac{Conc_{115} \text{ x } Area_{118(average)}}{Conc_{118} \text{ x } Area_{115}} = \mathbf{2.965}$$

In this limited sample, the average response factor was based on the average of four points. The area from injection #2 was not used. We then used the average response factor (2.965) to back calculate for DEM_{160} (fragment m/z=115) and the results are shown in Table 13. Using the following formula: $Conc_{115}=RRf*A_{115}*conc_{118}/A_{118}$.

Table 13. Recoveries (ng) Using FA Calculations for m/z = 115 compared to m/z =11

	Result	Expected	% Recovery
inj 1	19.09	20	95%
inj 2	44.57	20	223%
inj 3	17.07	20	85%
inj 4	20.45	20	102%
inj 5	18.93	20	95%

The FA technique normalizes most injections except that of injection #2. This is contrary to results obtained by HER with FA analysis yielded a relative standard deviation of <20% across multiple injections and multiple instruments.

We further examined a different fragment from the same data. Here we compared fragment m/z=117 and used fragment m/z=117 in lieu of m/z=118) as the focusing agent. Results are shown in Table 13 using the following formula: $=RRf*A_{115}*conc_{117}/A_{117}$.

Table 14. Recoveries Using FA Calculations for m/z = 115 compared to m/z =117

	Result	Expected	% Recovery
inj 1	17.59372	20	88%
inj 2	23.99166	20	120%
inj 3	16.39637	20	82%
inj 4	20.83891	20	104%
inj 5	17.59849	20	88%

Surprissingly, the results are greatly improved. This is further proof that the ion trap is skewing the fragment ions dependent on the ion. Without further development of the ion trap algorithms, it is unlikely that field results could be corrected using FA with the Griffin.

5.0 DISCUSSION

Considerable work was conducted to examine the Griffin. The work was delayed considerably with equipment malfunction. Fortunatley we had the "460" and "465" model and were able to continue analysis with the "465" model. Furthermore, the thermal desorption unit was not found to work consistently and was bypassed by injection into the associated docking station port (TDI) as discussed above.

Initial experiments demonstrated that the ion trap did not perform consistently resulting in spectra that did not conform with NIST. However, this was inconsistent and the fragmentation ranged from spectra similar to NIST to those that appeared to be soft ionization resulting in heaver fragmentation. Additional work would be required to determine if this is concentration dependent.

Additionally, when the mixture of DEM isotopes was injected, DEM^{M+1} (MW 161) was not found. We attribute this to the operation of the ion trap. This phenomenon occurred under a variety of conditions (i.e. injection site, concentration, etc.). We are stymied as to the performance of the ion trap detector associated with this instrument. Other ion trap manufacturers have corrected for the performance of the ion trap to provide NIST compatible spectra. Literature confirms that ion traps should produce NIST compatable spectra[3,4].

Direct injection of replicates resulted in poor reproducibility. Finally, since the isotopes could not be separated, the FA treatment could not be applied successfully.

In conclusion:

1. Mass spectrum generated by the ion trap were inconsistent;
2. The Xsorber TD appliance failed;
3. One unit failed to successfully autotune
4. The area was shown to vary widely from the beginning of the day, dropping substantially by the end of day; and
5. Focusing Agent evaluation of the data resulted in mixed results

We conclude that there are serious flaws with Griffin that could not be resolved in this study. Our presumption is that the ion trap has difficulty with overlapping fragment ions. Unfortunately, the failure to capture isotopic curves does not lend the Griffin as a useful tube to capture data with a high degree of precision/accuracy as recently published for the HER[2].

6.0 REFERENCES

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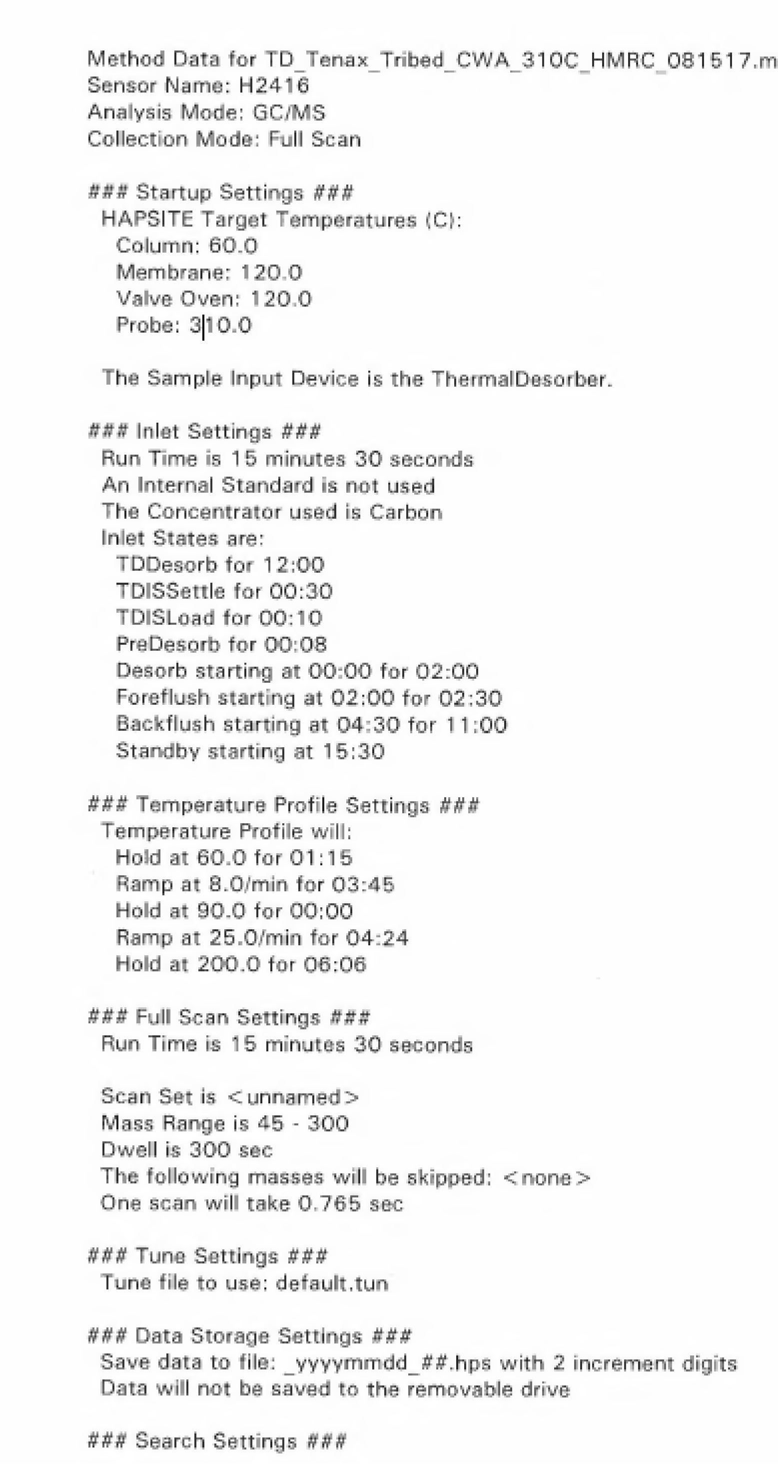
[2] A.V. Qualley, G. Hughes, H. M. Rubenstein. Data quality improvement for field-portable gas chromatography-mass spectrometry through the use of isotopic analogues for in-situ calibration. Env. Chemistry. https://doi.org/10.1071/EN19134 (on-line), 2019.

[3] Robert L. Fitzgerald, Carol L. O'Neal, Bradley J. Hart, Alphonse Poklis, and David A. Herold. Comparison of an Ion-Trap and a Quadrupole Mass Spectrometer using Diazepam as a Model Compound. Journal of Analytical Toxicology, Vol. 21, October 1997

[4] Hans-Joachim Huebschmann, Workhorses of the Chromatography Lab: Quadrupoles and Ion Traps, Thermo-Fisher,White Paper 10427

7.0 APPENDIX A – HAPSITE-ER METHOD CONFIGURATION



```
Method Data for TD_Tenax_Tribed_CWA_310C_HMRC_081517.mth
Sensor Name: H2416
Analysis Mode: GC/MS
Collection Mode: Full Scan

### Startup Settings ###
  HAPSITE Target Temperatures (C):
    Column: 60.0
    Membrane: 120.0
    Valve Oven: 120.0
    Probe: 310.0

  The Sample Input Device is the ThermalDesorber.

### Inlet Settings ###
  Run Time is 15 minutes 30 seconds
  An Internal Standard is not used
  The Concentrator used is Carbon
  Inlet States are:
    TDDesorb for 12:00
    TDISSettle for 00:30
    TDISLoad for 00:10
    PreDesorb for 00:08
    Desorb starting at 00:00 for 02:00
    Foreflush starting at 02:00 for 02:30
    Backflush starting at 04:30 for 11:00
    Standby starting at 15:30

### Temperature Profile Settings ###
  Temperature Profile will:
    Hold at 60.0 for 01:15
    Ramp at 8.0/min for 03:45
    Hold at 90.0 for 00:00
    Ramp at 25.0/min for 04:24
    Hold at 200.0 for 06:06

### Full Scan Settings ###
  Run Time is 15 minutes 30 seconds

  Scan Set is <unnamed>
  Mass Range is 45 - 300
  Dwell is 300 sec
  The following masses will be skipped: <none>
  One scan will take 0.765 sec

### Tune Settings ###
  Tune file to use: default.tun

### Data Storage Settings ###
  Save data to file: _yyyymmdd_##.hps with 2 increment digits
  Data will not be saved to the removable drive

### Search Settings ###
```