The stability of Tenax TA thermal desorption tubes in simulated field conditions on the HAPSITE® ER

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Due to the growing need to monitor aircraft cabin, cockpit and breathing-line air quality, functional assessment of sampling equipment for the specialised field conditions of flight need to be established for both in-flight and ground safety. In this article, we assess the reliability of Tenax TA thermal desorption tubes to perform under various relevant field sampling conditions, such as storage temperature, loading temperature, vibrational velocity, gravitational force (G Force) and altitude pressure with semi-real-time gas chromatograph-mass spectrometer (GC-MS) analysis on the field portable HAPSITE® ER (Hazardous Air Pollutants on Site Extended Range) instrument. First, we show that Tenax TA thermal desorption tubes can handle storage under extreme environmental conditions, 4–77°C, over numerous analytical test cycles. Next, we confirm that extreme loading temperature, both hot (77°C) and cold (4°C), does not affect the analytical reliability of Tenax TA thermal desorption tubes. Then, we illustrate that G Force may have a significant \( p \leq 0.0364 \) effect on Tenax TA performance while vibrational velocity \( p \leq 0.7265 \) and low ambient air pressure \( p \leq 0.1753 \), such as that found at high altitude, do not. Finally, several Tenax TA thermal desorption tubes were flight-tested, demonstrating that the durability of these tubes maybe insufficient for use on military cargo aircraft \( p = 0.0107 \). The results presented here provide a rationale for additional testing of Tenax TA thermal desorption tubes for flight suitability.

Keywords: Tenax TA; HAPSITE® ER; thermal desorption; flight; air quality

1. Introduction

Questions about the quality of air supplied in commercial and military aircraft have raised significant health and safety concerns around the aviation community \([1,2]\). The concerns largely stem from the use of potentially contaminated re-circulated air, from cooled engine bleed air, for cabin and cockpit breathing air supply. For instance, Bagshaw estimated that 1 in 2000 flights will have a ‘fume event’, characterised by smoke or fumes in the pressurised cabin \([3]\). Such events have caused an estimated 324 total in-flight events, resulting in in-flight diversions and 121 ground-based events leading to delays and cancellations over an 18-month time period \([4]\). As a result, commercial flight crews have reported a number of symptoms including weakness, dizziness, nausea, vomiting and headache \([2]\). Air quality sampling of both commercial and military aircraft has shown the presence of contaminants that could result in the observed symptomology.

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For example, DeNola et al. found concentrations of the neurotoxin tricresyl phosphate in the low parts-per-trillion range from samples collected from aircraft [5]. While extremely useful, all of the analyses in these studies were conducted at an off-site laboratory, such that near-real-time detection and subsequent exposure mitigation protocols could not be implemented in a timely manner. These potential health risks support the need for monitoring air quality for contaminants such as volatile organic compounds (VOCs) in near-real time during flight and ground engine runs.

Real-time or semi-real-time detection of hazardous compounds in the air requires portable, sensitive onsite detection. The Hazardous Air Pollutants on Site (HAPSITE®), a field portable gas chromatograph-mass spectrometer (GC-MS) with thermal desorption (Extended Range (ER) model) and NIST Library search capabilities, is a promising candidate to fill this role. The HAPSITE® ER allows for portable—able to be carried on an individual’s back—near-real-time GC-MS capabilities through an easy to operate interface. Although not currently used in flight due to the large expense to purchase and the weight and potential damage that may occur, the HAPSITE® has been used in field sampling of VOCs in various ground-based environments [9–21].

As an alternative to in-flight HAPSITE® analysis, thermal desorption (TD) tube sampling for collection of VOCs in flight, with later immediate ground analysis on the HAPSITE® ER, can provide a light, cost-effective, near-real-time, analysis of air quality. TD tube analysis is an attractive air sampling technique because it enhances sensitivity by concentrating airborne volatiles within the tube, does not require solvent extraction and a multitude of sorbents are available with different VOC adsorption properties. Tenax TA is one of the most widely used adsorbent materials for TD VOC collection [22,23]. Tenax TA, a porous polymer of poly-2,6-diphenyl-1,4-phenylene oxide, has been used since the mid-1980s for sampling VOCs from various sources. The hydrophobic nature of Tenax TA avoids the water-derived (i.e., humidity) analytical issues experienced with carbon or multi-bed TD material while still retaining a large range of compound capture (C₆–C₃₀), though sorptive loss of semi-volatiles has been associated with stainless steel Tenax tubes [22,24–26]. Though substantial effort has been placed on compound storage and stability on Tenax TA TD tubes in normal laboratory sampling conditions, very little is known about how Tenax TA performs in extreme field sampling conditions, such as those observed in flight, temperature, altitude, G force and vibrational force [27,28].

The purpose of this work was to assess the ability of Tenax TA to adsorb and desorb two TO-14A internal standard (IS), compounds (bromofluorobenzene (BFB), chlorobenzene-d₅ (CB)) under various stress conditions related to field sampling such as storage temperature, loading temperature, vibrational velocity, gravitational force (G Force) and altitude pressure with simulated semi-real-time analysis on the field applicable to the HAPSITE® ER instrument. The results presented in this article establish the need for further testing of Tenax TD tubes for flight suitability for monitoring air quality in flight.

2. Experimental
2.1. Reagents
HAPSITE® internal standard, 50 ppb bromopentafluorobenzene and 1,3,5-tris(trifluoromethyl) benzene, Inficon Inc., Bad Ragaz, Switzerland. TO-14A internal standard/tuning mix, 100 ppb each bromochloromethane, 4-bromofluorobenzene, chlorobenzene-d₅, 1,4-difluorobenzene, Linde Gas North America, Stewartsville, NJ, USA. See Table 1 for physical, chemical and experimental properties.
Table 1. Summary of physical, chemical and experimental properties of target VOCs.

| Compound                  | CAS #     | Molecular Weight (g/mol) | Boiling Point (°C) | Vapour Pressure (mmHg) |
|---------------------------|-----------|--------------------------|--------------------|------------------------|
| Bromochloromethane        | 74–97-5   | 128                      | 68                 | 117**                  |
| Chlorobenzene-d5          | 3114–55-4 | 117                      | 130                | 12*                    |
| 4-Bromofluorobenzene      | 460–00-4  | 174                      | 152–155            | 4*                     |
| 1,4-Difluorobenzene       | 540–36-3  | 114                      | 88–89              | 64*                    |

| Compound                  | Stock Concentration | Stock Phase | Volume Sampled | Amount Loaded          | Supplier   |
|---------------------------|---------------------|-------------|----------------|------------------------|------------|
| TO-14A IS Mix             | 100 ppb each compound | Gas         | 25 mL          | 2.5 ppm each compound  | Restek     |

Note: *At 25°C; **at 20°C.
2.2. **Thermal desorption sorbent tubes**

Tenax TA (35/60 mesh) stainless steel thermal desorption (3.5’ × ¼’) tubes were obtained from Markes International, South Wales, UK, and Supelco, Bellefonte, PA, USA. The single sorbent tubes were conditioned prior to initial analysis as described by the manufacturers. Briefly, the Tenax TA thermal desorption tubes were loaded into a TC-20 conditioner, Markes International. Under constant nitrogen pressure (99.999% pure, 206.8 kPa), tubes were heated to 320°C and held for 2 h. The TD tubes were brought to room temperature under nitrogen pressure, and brass storage caps with polytetrafluoroethylene ferrules were affixed to each end. All tubes remained capped when not under analysis and were reconditioned after each analysis, unless otherwise specified.

2.3. **HAPSITE® ER analysis**

Stainless steel Tenax TA thermal desorption tubes were manually loaded with 25 mL (2.5 ppm) of TO-14A internal standard/tuning mix gas using a modified Markes Calibration Solution Loading Rig, Markes International, backed with constant nitrogen at 124.1 kPa (99.999%) and a 50 mL Gastight syringe (Hamilton Co, Reno, NV, USA). The TO-14A gas mix was injected over a 10-s period, with the syringe remaining in the loading rig for an additional 10 s after all the IS mix had been injected. Breakthrough was determined by detection of TO-14A IS compounds on an additional Tenax TA thermal desorption tube in line with, but following, the TD tube being loaded [29]. To simulate semi-real-time detection, GC-MS analysis was conducted on a HAPSITE® ER portable chemical identification system equipped with the HAPSITE® thermal desorption accessory, Inficon Inc., East Syracuse, NY, USA. Gaseous HAPSITE® Internal Standard was automatically loaded, by the HAPSITE ER, onto the Tri-Bed concentrator before each injection. The HAPSITE® ER was internally fitted with a 100% polydimethylsiloxane, 15 m × 0.25 mm ID, 1.0-μm df GC column using nitrogen carrier gas under constant pressure (88 kPa). Thermal desorption occurred at from 40°C to 316°C over 5 min. Compounds were concentrated on the Tri-Bed concentrator and predesorbed for 8 s and completely desorbed for 30 s at approximately 300°C. Gas chromatography was carried out with the initial settings: 60°C column temperature, 80°C membrane temperature, 70°C Valve Oven temperature and 300°C Probe temperature. Following a 1-min hold at 60°C, the column temperature was increased linearly to 80°C at 6°C/min, 120°C at 12°C/min and 180°C at 26°C/min. The total GC runtime was 10 min. Mass spectra were obtained by electron impact ionisation at 70 eV with a mass scan range of 45–300 m/z at a scan rate of 0.765 scans/s and a dwell time of 300 s. Spectra were manually inspected for ion intensities using the HAPSITE® ER IQ PC application (v. 2.32) Inficon Inc., East Syracuse, NY, USA.

2.4. **Statistical analysis**

All raw and HAPSITE internal standard #2 (bromopentafluorobenzene) normalised ion intensities are provided in Supplemental Data 1. Statistical analyses were conducted in Prism GraphPad software, GraphPad Software Inc., La Jolla, CA. All analyses assumed an α = 0.05.

3. **Results and Discussion**

3.1. **Stability of Markes Tenax TA tubes across temperatures**

Tenax TA is one of the most popular adsorbent materials used for VOC analysis due to its ability to adsorb a wide range of volatile analytes with minimal affect from background water
Compound stability and storage on Tenax TA, at various temperature conditions (4–40°C) and durations (up to 12 months), has been previously studied [27,30]. However, the effect of long-term storage of Tenax TA TD tubes with regard to extreme high and low temperature on the later adsorption and desorption of compounds has not previously been reported. To address this concern, we used the Restek TO-14A internal standard gas mix consisting of 100 ppb each bromochloromethane, 4-bromofluorobenzene (BFB), chlorobenzene-d5 (CB) and 1,4-difluorobenzene. The TO-14A IS was selected due to its availability, the relatively few number compounds leading to quick analysis, adequate GC separation of the mixture and a low observation of carryover in the HAPSITE® ER system. These attributes, in addition to the established use of chlorobenzene on Tenax TA, made the TO-14A gas mixture an ideal standard material for this study [30]. Furthermore, loading of the TO-14A IS mix was performed using a 50-mL Hamilton gas-tight syringe as an alternative to the more standard vacuum pump commonly used for Tenax TA TD tube loading. This method ensures a more consistent and reproducible loading of the IS compounds, although some sample loss by similar methodology has been noted [31].

The adsorption and desorption of the TO-14A IS compounds on Tenax TA TD tubes, stored at extreme field applicable temperatures, were tested over time by placing brand new, reconditioned, Markes Tenax TA TD tubes at room temperature (21°C or 70°F, \( n = 5 \)), extremely high temperature (77°C or 170°F, \( n = 5 \)) and extremely low temperature (−20°C or −4°F, \( n = 4 \)), etc., runways in the desert or arctic. Prior to each analysis, tubes were equilibrated to room temperature, loaded with 25 mL (2.5 ppm) of TO-14A internal standard (IS) and run on the HAPSITE® ER instrument. Following analysis, TD tubes were reconditioned, as described previously, and returned to the applicable storage conditions. The TD tubes were analysed and reconditioned, considered one complete analytical cycle, once a week for 15 consecutive weeks (15 total cycles). Storage temperatures (thermometer PNs: 13202583, 13202589, 13202635, Fisherbrand, Pittsburgh, PA, USA) and laboratory percentage relative humidity (%RH; SHT21, Sensiron, Switzerland) were noted daily, during the workweek, and have been provided in Supplemental Data 2.

Chlorobenzene-d5 and BFB were selected from the TO-14A IS mixture for monitoring due to the increased abundance in the HAPSITE ER, compared to the other two compounds, bromochloromethane and difluorobenzene, in laboratory test injections (data not shown). Representative total ion chromatograms (TICs) of each temperature over the entire testing period are provided in Supplemental Data 3. The ion abundances (CB m/z 82 and BFB m/z 95) were normalised to the HAPSITE® internal standard #2 (bromopentafluorobenzene) ion abundance (m/z 167), for each injection, to account for instrumental variability. Normalised values were plotted as a function of time. Figure 1A and 1B depict the mean IS normalised ion abundances for CB and BFB when stored at the various temperature conditions. The data show stable detection of both CB and BFB over the 15-cycle testing period at each test temperature (Figure 1A and 1B). Additionally, the performance of the tubes (i.e., mean normalised abundance), regardless of storage condition, was not statistically different over the duration of the experiment (CB \( p = 0.2984 \), BFB \( p = 0.1406 \), by one-way ANOVA). However, the increased storage temperature (77°C) did induce a consistent and significant \( (p = 0.0004, \text{by one-way ANOVA}) \) increase in the mean normalised abundance of benzaldehyde (m/z 106) detected (Tenax TA bleed compound) when compared to the decreased (−20°C) and room temperature (21°C) storage conditions (Figure 1C) [32]. These results indicate benzaldehyde maybe a contaminant with the potential to interfere with analytes of interest when stored at elevated temperatures.

Collectively, these data suggest Tenax TA thermal desorption tubes can be stored for longer than 3 months at extreme temperature conditions while retaining functionality in the HAPSITE® ER instrument, similar to tubes stored at room temperature. Although the
Figure 1. The stability of Tenax TA TD tube over time under various storage temperatures and manufacturers.
Plots of the normalised replicate ion abundances from Markes Tenax TD tubes stored at high, low and room temperature (77°C n = 5, −20°C n = 4, 21°C n = 5). (A) CB (m/z 82), (B) BFB (m/z 95), (C) Benzaldehyde (m/z 106). Plots of the replicate CB ion abundances (m/z 82) from Tenax TD tubes, stored at ambient temperature (21°C), from different manufacturers (Markes and Supelco, n = 5 each manufacturer). (D) CB (m/z 82), (E) BFB (m/z 95). (F) benzaldehyde (m/z 106). All error bars represent the 95% confidence interval (CI).
HAPSITE® ER thermal desorption process is more gentle than that of other instruments as described in Section 2, our results are in line with other storage and stability studies of Tenax TA, whereas our data was collected under more controlled conditions [33,34]. Our results establish a minimum number of analyses and recondition cycles (15 complete analytical cycles) over an extended range of temperatures. Tenax TA thermal desorption tubes can be used without a significant loss in performance on the HAPSITE® ER instrument under controlled conditions.

3.2. Comparison of Tenax TA tubes acquired from different manufacturers

Many comparisons of Tenax TA material to carbon-based sampling media have been made; however, the performance comparison of different Tenax TA tube manufacturers has not been described [23,35–37]. To determine whether the difference in manufacturer of the thermal desorption tube has any effect on the results, TO-14A IS adsorption and desorption over time or differences in background, five additional stainless steel Tenax TA TD tubes were custom ordered from Supelco® (35/60 mesh). The custom TD tubes were stored at room temperature with the five comparable Markes TD tubes, loaded with TO-14A IS and run on the HAPSITE® ER once a week, as described previously. Representative TICs, raw and normalised ion abundances are provided in Supplemental Data 1 and 4. Figure 1D and 1E shows the mean IS normalised ion intensities for CB and BFB from both manufacturers, Markes and Supelco, over the 15-week test period. As expected, each manufacturer’s TD tubes performed similarly, in the HAPSITE® ER, over the entire time course (CB $p = 0.4766$, BFB $p = 0.1803$, Student’s t-test). However, unexpectedly, the Supelco TD tubes showed a significantly ($p = 0.0038$, Student’s t-test) higher amount of benzaldehyde than those manufactured by Markes (Figure 1F). Although availability of the Supelco Tenax TA tubes limited the analysis to only room temperature storage, these results suggest TO-14A IS adsorption and desorption are similar across the tubes from two different manufacturers. Additionally, these data highlight the need to assess the background of laboratory consumables, such as thermal desorption tube benzaldehyde, for sensitive analyses.

3.3. Effect of high and low temperature loading on compound adsorption and desorption

While the data shown in Figure 1 suggest storage temperature has little effect on the adsorption and desorption of the TO-14A compounds, we sought to confirm the temperature dependence of TD tube temperature on sample loading, i.e., breakthrough [38]. To simulate sampling in extremely hot and cold environments, i.e., in airplanes parked on runways in the desert and the arctic, we placed five Markes Tenax TA TD tubes at room temperature (21°C or 70°F) and the extremes of environmental temperatures (−20°C and 77°C, −4°F and 170°F, respectively) for 24 h. Tubes were individually removed from storage conditions and immediately loaded with 25 mL TO-14A IS at room temperature, while collecting compound breakthrough on a second in line Tenax TA thermal desorption tube, with both tubes run on the HAPSITE® ER, as described previously. Representative ion chromatograms and raw ion abundances are provided in Supplemental Data 1 and 5. Figure 2A, 2B, 2E, and 2F shows the replicate ion abundances for CB and BFB for each loading temperature. The high loading temperature, representative of extreme desert conditions, showed no significant difference (Student’s t-test) in the ability to adsorb CB ($p = 0.0749$) and BFB ($p = 0.0761$), illustrated by minimal breakthrough, when compared to the room temperature loading (Figure 2A and 2B). However, when a single positive control Tenax TA TD tube was placed at 154°C (309°F, well above any temperature observed on Earth), immediately loaded with TO-14A IS and analysed, a reduced ability to
Figure 2. Effect of loading temperature on Tenax TA TD tube compound adsorption and thermal desorption.
Scatter plots of the replicate ion abundances from Tenax TD tubes loaded at high temperature (21°C n = 5, 77°C n = 5, 154°C n = 1). (A) CB (m/z 82). (B) BFB (m/z 95). (C) Representative ion chromatograms for breakthrough of CB when Tenax TD tubes were loaded under high temperature. (D) A scatter plot of the ion abundances for CB and BFB breakthrough when Tenax TD tubes were loaded under high temperature. Scatter plots of the replicate ion abundances from Tenax TD tubes loaded at low temperature (21°C n = 5, −20°C n = 5, −80°C n = 1). (E) CB (m/z 82). (F) BFB (m/z 95). NS, not significant. Error bars represent the 95% CI. Percentage values indicate the %RSD.
adsorb both CB and BFB was observed, shown by an increase in IS compounds detected on the breakthrough TD tube (Figure 2C, 2D and Supplemental Data 5).

Conversely, when Tenax TA TD tubes are stored and loaded at low temperatures, simulating arctic sampling conditions, an increased ability to adsorb IS compounds was observed (Figure 2E and 2F). Only CB showed a statistically significant ($p = 0.0025$, Student’s $t$-test) increase in compound detection when compared to room temperature loading (Figure 2E). However, this observation can be attributed to a potential outlier in the BFB dataset at $-20^\circ$C. For example, if the lowest value for BFB at $-20^\circ$C is removed, the results have a statistically significant difference ($p = 0.0029$, Student’s $t$-test) in ion abundance between the room temperature and the $-20^\circ$C loading. The increase in compound detection was also observed with a positive control Tenax TA TD tube stored at $-80^\circ$C ($-112^\circ$F, Figure 2E and 2F), although this temperature is well below any observed on Earth. Additionally, no Tenax TD tube loaded at low temperature showed any detectable IS compounds on the breakthrough TD tubes (Supplemental Data 5).

These results, although limited in the number of compounds tested, can be extrapolated to a number of other compounds with similar physical characteristics and direct applicability to in-flight HAPSITE ER detection. For example, the boiling point and vapour pressure of the nerve agent Sarin is 147°C and 2.9 mmHg at 25°C, respectively [39]. These properties are similar to those of the compounds tested in our experimentation, CB and BFB (Table 1). As a result, we would expect these data to be applicable to sampling the nerve agent Sarin, or other compounds with comparable physical properties, under similar conditions.

The data presented here are not in agreement with the previous observation by Kroupa et al. showing the temperature dependence of VOC breakthrough via microtrap technology [38]. This discrepancy can be attributed to the increased temperature tested, up to 170°C, and large range of volatility of the analytes (approximately 6 mmHg at 20°C for m-xylene to 17,600 mmHg at 24°C for 1-hexene), in addition to the TD tube used in the Kroupa et al. experiments [38]. We hypothesise that the analytes loaded at 154°C were sufficiently hot enough to observe the breakthrough response similar to those observed by Kroupa et al. However, testing such a hypothesis was beyond the scope of this study. Collectively, our results suggest that, under the most extreme temperature conditions found on Earth, Tenax TA TD tubes can be sampled and analysed on the HAPSITE® ER with minimal breakthrough of the TO-14A IS compounds.

3.4. Effect of G force on compound adsorption and desorption

Due to the emerging realisation that air quality should be monitored in both commercial and military aircraft, it is necessary to understand the performance of thermal desorption tubes under gravitational (G) force. To test the influence of G force on Tenax TA TD tube compound adsorption and thermal desorption, we centrifuged four Markes Tenax TA TD tubes at 19g for 3 min at room temperature on a Thermo Sorvall Legend RT swinging bucket centrifuge (Thermo Scientific, Waltham, MA). Although 19g is well above the G force observed in-flight (typically brief stints of less than 7g for military aircraft and significantly less for commercial flights), this is the lowest G force attainable in our laboratory. Therefore, we were limited to 19g for our analysis. Additionally, due to acceleration and deceleration in the centrifuge, 3 min was the most applicable test duration. Following centrifugation, centrifuged and non-centrifuged (0g) tubes were manually loaded with TO-14A IS, while collecting breakthrough, and analysed on the HAPSITE® ER instrument, as described previously. Representative ion chromatograms and raw ion abundances are provided in Supplemental Data 1 and 6. G force (19g) had a negative effect on the detection of CB and BFB when compared to those tubes that were not centrifuged (Figure 3A–3D). A statistically significant reduction, by Student’s $t$-test, in the CB
Figure 3. Effect of G force on Tenax TA TD tube compound adsorption and thermal desorption. Representative extracted ion chromatograms across variable G forces. (A) CB (m/z 82). (B) BFB (m/z 95). Scatter plots of the replicate ion abundances from variable vibrational velocities (0g n = 5, 19g n = 4, 100g n = 2). (C) CB (m/z 82). (D) BFB (m/z 95). (E) Representative ion chromatogram for BFB when Tenax TD tubes were re-analysed without prior reconditioning. (F) A scatter plot of the ion abundances for CB and BFB when re-analysed without prior reconditioning. Error bars represent the 95% CI. Percentage values indicate the %RSD.
(p = 0.0184) and BFB (p = 0.0364) ion abundances were observed with the application of G force to the tubes. As expected, the reduction in ion abundance was further intensified when positive control tubes were centrifuged at 100g (Figure 3A–3D). Interestingly, the reduced ion abundances found in those tubes put under G force were not due to limited compound adsorption, i.e., breakthrough (Supplemental Data 6). Rather, the compounds, when the TD tubes were reanlysed without prior reconditioning, remained bound to the sorbent in those tubes that were centrifuged (Figure 3E, 3F and Supplemental Data 6). We hypothesise this is a result of Tenax TA compaction either obscuring the flow path or reducing the thermal desorption process. These results suggest G force has a negative effect on desorption of compounds from Tenax TA thermal desorption tubes in the HAPSITE® ER. However, the minimal gravitational force and duration tested, yielding this conclusion, was beyond that observed in routine commercial or military flight. These data indicate further testing is required to adequately evaluate those G forces more applicable to manned flight.

3.5. Effect of vibrational velocity on compound adsorption and desorption

Thermal desorption tubes have the potential to encounter extreme vibrational forces during ground and air transport and field sampling. To test the influence of vibrational force on the ability for Tenax TA thermal desorption tubes to adsorb and desorb TO-14A IS compounds in the HAPSITE® instrument, we placed four (two per set), tubes on a Fisher Scientific mini-vortexer (Pittsburgh, PA) for 1 h at room temperature. The vibrational velocity was measured using a Reed SD-8205 vibration meter (Reed Instruments, Niagra Falls, NY). See Supplemental Data 7 for vibrational velocity data. The mean low vibrational velocity was 0.016 m/s (mean of two sets) while the high vibrational velocity (positive control) was 0.055 m/s. Following vibrational stress, vibrated and non-vibrated (0 m/s), tubes were manually loaded with 25 mL of IS, while collecting breakthrough, and analysed on the HAPSITE® ER. Representative ion chromatograms and raw abundances are provided in Supplemental Data 1 and 7. The data shows vibrational velocity has an insignificant effect on Tenax TA TD tube capture and desorption of IS compounds (Figure 4A–4D). Although CB shows a slight reduction in ion intensity with increased vibrational velocity, these results are not significant by a Student’s t-test (p = 0.0741, Figure 4C). Furthermore, vibrations showed no detectable evidence of induced IS compound breakthrough (Supplemental Data 7). The positive control TD tube exposed to the extremely high vibrational velocity (0.055 m/s) showed a slight reduction in CB and BFB ion abundances, but statistical analysis was impossible on a single replicate sample. Collectively, these results propose vibrational velocity may affect Tenax TD tube performance at extremely high vibrational velocities, but further research is necessary to confirm these preliminary results.

3.6. Effect of altitude on compound adsorption and desorption

Commercial and cargo aircraft are pressurised; however, the threat of cabin depressurisation always exists. To determine whether Tenax TA thermal desorption tubes can withstand a loss of cabin pressure, three TD tubes were placed in a custom altitude chamber and taken up to a simulated altitude of 25,000 ft for 15 min [40–42]. Altitude profiles are provided in Supplemental Data 8. Altitude pressure exposed and non-exposed tubes were manually loaded, following stressed conditions, with 2.5 ppm IS, while collecting breakthrough, and run on the HAPSITE® ER as described previously. Representative ion chromatograms and raw abundances are provided in Figure 5A, 5B and Supplemental Data 1. As shown in Figure 5C and 5D altitude had an insignificant effect on the ion abundances of CB (p = 0.09866) and BFB (p = 0.1753) by a Student’s t-test. Additionally, no IS compound breakthrough was detected in any exposure
group even the positive control tube, exposed to 60,000 ft (Supplemental Data 8). These results show altitude has little effect on the adsorption and desorption capacity of Tenax TA thermal desorption tubes in the HAPSITE® ER analysis. Furthermore, the data supports the use of Tenax TA TD tubes for high-altitude sampling.

3.7. Effect of flight on compound adsorption and desorption

Ultimately, the goal of monitoring in-flight air quality requires sampling media to withstand the collective and simultaneous effects of the simulated flight conditions. To test whether Tenax TA thermal desorption tubes can withstand flight, five Tenax TD tubes were taped onto the floor of a C17 military cargo aircraft for a 205-min flight reaching altitudes of up to 35,000 ft. At this location, the TD tubes experienced all the tested simulated effects simultaneously. Following the flight, the tubes were collected, manually loaded with 2.5 ppm IS and analysed via the HAPSITE® ER. Tenax TA TD tubes stored on the shelf in our laboratory were used as control.

Figure 4. Effect of vibrational velocity on Tenax TA TD tube compound adsorption and thermal desorption.

Representative extracted ion chromatograms across variable vibrational velocities. (A) CB (m/z 82). (B) BFB (m/z 95). Scatter plots of the replicate ion abundances from variable vibrational velocities (0 m/s n = 5, 0.016 m/s n = 4, 0.055 m/s n = 1). (C) CB (m/z 82). (D) BFB (m/z 95). NS, not significant. Error bars represent the 95% CI. Percentage values indicate the %RSD.
Representative ion chromatograms and raw abundances are provided in Figure 6A, 6B and Supplemental Data 1. Figure 6C and 6D shows plots of replicate ion abundances for CB and BFB. These data show that flight conditions have a potential significant effect, when compared to those stored in the laboratory, on the measured abundances of CB and BFB. First, there was a significant increase, by a Student’s t-test, in the abundances of BFB ($p = 0.0107$) following flight. Additionally, while not statistically significant, CB ($p = 0.0869$) also showed an increase in the measured abundances after TD tubes were flown in the C17 aircraft. Finally, there was a greater variability in the repeated measurements, shown by %RSD, for both CB and BFB in tubes that were placed in the aircraft (Figure 6C and 6D).

These data suggest that Tenax TA thermal desorption tubes may be effected by flight conditions in cargo aircraft. Although the laboratory studies of Tenax stability show a decrease, or no effect, in abundance when placed under individualised stress, the flight data suggests the reverse. We hypothesise the increased abundance observed from the in-flight data is a result of an exceedingly large amount vibrational force applied to the Tenax tubes during the C17 flight. The vibrational velocity, applied to the tubes during flight, could cause the Tenax material to

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Figure 5. Effect of altitude on Tenax TA TD tube compound adsorption and thermal desorption. Representative extracted ion chromatogram across to variable altitudes. (A) CB (m/z 82). (B) BFB (m/z 95). Scatter plots of the replicate ion abundances from variable altitudes (0 ft $n = 3$, 25,000 ft $n = 3$, 60,000 ft $n = 1$). (C) CB (m/z 82). (D) BFB (m/z 95). NS, not significant. Error bars represent the 95% CI. Percentage values indicate the %RSD.
shear, creating an increased surface area allowing for a more complete desorption profile of the TO-14A IS compounds. However, additional tests will be necessary to confirm this hypothesis and further elucidate what specific attribute causes the differences observed when compared to laboratory storage.

4. Conclusion
With increasing concern for the quality of air provided to passengers and crew of both commercial and military aircraft, the need for in-flight monitoring of air quality is of utmost importance for the safety of those in the air and on the ground. While in-flight testing of the HAPSITE® durability and functionality may occur in the near future, alternative methods for air quality assessments are currently required. Although thermal desorption tubes have been used to monitor commercial flights previously, it is uncertain how the data would be affected by the sampling conditions in flight [43]. Furthermore, no data currently exists for the use of thermal desorption tube sampling in conditions associated with military flight profiles, such as high

Figure 6. Effect of flight on Tenax TA TD tube compound adsorption and thermal desorption. Representative extracted ion chromatogram exposed to C17 flight conditions. (A) CB (m/z 82). (B) BFB (m/z 95). Scatter plots of the replicate ion abundances from flight conditions (lab n = 5, flight n = 5). (C) CB (m/z 82). (D) BFB (m/z 95). NS, not significant. Error bars represent the 95% CI. Percentage values indicate the %RSD.
vibrational velocity. Although the data presented in this article is not absolute in its quantitation of the TO-14A IS compounds, as shown in numerous other studies on TD tube thermal desorption, we have shown, using relative quantitation, that Tenax TA TD tubes perform well when stored under extreme temperature [25,26,29,31,44,45]. Additionally, we have established the first data testing the functionality of Tenax TA thermal desorption tubes under extreme field conditions with subsequent analysis on the highly relevant HAPSITE® ER portable GC-MS system. Finally, we demonstrate the effects of a C17 flight on Tenax TA TD tube compound retention. All results are summarised in Supplemental Data 9. Collectively, these data illustrate the need for further testing of Tenax TA TD tubes, for in-flight monitoring of air quality for VOC contaminants, with on-site HAPSITE® ER analysis for near-real-time detection.

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Supplemental data
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References
[1] J. Sullivan, D. Bush and S. Bousum, (2012). <http://www.gpo.gov/fdsys/pkg/CHRG-112hhrg76215/pdf/CHRG-112hhrg76215.pdf>
[2] R. Harrison, J. Murawski, E. McNeely, J. Guerriero and D. Milton, Exposure to Aircraft Bleed Air Contaminants Among Airline Workers: A Providers (2009). <http://ashsd.afacwa.org/docs/HCPfull.pdf>
[3] M. Bagshaw, Health Effects of Contaminants in Aircraft Cabin Air (2014). <http://www.asma.org/asma/media/asma/Travel-Publications/Air-contamination-health-effects-report-v2-7-Apr2014.pdf>
[4] J. Murawski and D.S. Supplee, J. ASTM Int. 5, JA1101640 (2008). doi:10.1520/JAI101640.
[5] G. DeNola, P.J. Hanhela and W. Mazurek, Ann. Occup. Hyg. 55, 710 (2011). doi:10.1093/annhyg/mer040.
[6] P.J. Hanhela, J. Kibby, G. DeNola and W. Mazurek Organophosphate and Amine Contamination of Cockpit Air in the Hawk, F-111 and C-130 Aircraft (2005). <http://oai.dtic.mil/oai/oai?verb=getRecord&metadataPrefix=html&identifier=ADA448000>
[7] M. Liyasova, B. Li, L.M. Schopfer, F. Nachon, P. Masson, C.E. Furlong and O. Lockridge, Toxicol. Appl. Pharmacol. 256, 337 (2011). doi:10.1016/j.taap.2011.06.016.
[8] J.D. Pleil, L.B. Smith and S.D. Zelnick, Environ. Health Perspect. 108, 183 (2000). doi:10.1289/ehp.00108183.
[9] D. Blake, A.L. Hinwood and P. Horwitz, Chemosphere 76, 419 (2009). doi:10.1016/j.chemosphere.2009.03.047.
[10] J.R. Kastner and K.C. Das, J. Air Waste Manage. 52, 459 (2002). doi:10.1080/10473289.2002.10470800.
[11] S. Kim, T. Karl, A. Guenther, G. Tyndall, J. Orlando, P. Harley, R. Rasmussen and E. Apel, Atmos. Chem. Phys. 10, 1759 (2010). doi:10.5194/acp-10-1759-2010.
[12] M. Moalemiyan, A. Vikram and A.C. Kushalappa, Postharvest Biol. Technol. 45, 117 (2007). doi:10.1016/j.postharvbio.2006.08.020.
[13] M. Moalemiyan, A. Vikram, A.C. Kushalappa and V. Yaylayan, Plant Pathol. 55, 792 (2006). doi:10.1111/j.1365-3059.2006.01443.x.
[14] B. Prithiviraj, A. Vikram, A.C. Kushalappa and V. Yaylayan, Eur. J. Plant Pathol. 110, 371 (2004). doi:10.1023/B:EPJP.000021058.81491.f8.
[15] A. Vikram, L.H. Lui, A. Hossain and A.C. Kushalappa, Ann. Appl. Biol. 148, 17 (2006). doi:10.1111/j.1744-7348.2005.00036.x.
[16] A. Vikram, B. Prithiviraj and A.C. Kushalappa, J. Plant Pathol. 86, 215 (2004).
[17] A. Vikram, B. Prithiviraj, H. Hamzehzarghani and A.C. Kushalappa, J. Sci. Food Agric. 84, 1333 (2004). doi:10.1002/jsfa.1828.
[18] A. Vikram, H. Hamzehzarghani and A.C. Kushalappa, Can. J. Plant Pathol. 27, 194 (2005). doi:10.1080/07060660509507216.
[19] T. Zarra, V. Naddeo and V. Belgiorno, Global NEST J. 11, 477 (2009).
[20] T. Zarra, V. Naddeo and V. Belgiorno, Chem. Eng. Trans. 15, 63 (2008).
[21] P. Kolar, J.R. Kastner and J. Miller, Appl. Catal B-Environ. 76, 203 (2007). doi:10.1016/j.apcatb.2007.05.022.
[22] C.A. McCaffrey, J. MacLachlan and B.I. Brookes, Analyst 119, 897 (1994). doi:10.1039/an9941900897.
[23] M.P. Baya and P.A. Siskos, Analyst 121, 303 (1996). doi:10.1039/an99621000303.
[24] D. Helmig and L. Vierling, Anal. Chem. 67, 4380 (1995). doi:10.1021/ac00119a029.
[25] Y.-H. Kim, K.-H. Kim, J.E. Szulejko and D. Parker, Anal. Chem. 86, 6640 (2014). doi:10.1021/ac501382e.
[26] Y.-H. Kim and K.-H. Kim, Anal. Chem. 85, 7818 (2013). doi:10.1021/ac401385m.
[27] R.J. Peters and H.A. Bakkeren, Analyst 119, 71 (1994). doi:10.1039/an994190071.
[28] R.H. Brown and C.J. Purnell, J. Chromatogr. A 178, 79 (1979). doi:10.1016/S0021-9673(00)89698-3.
[29] K.-H. Kim, M.-H. Lee and J.E. Szulejko, Analyst 135, 46 (2014). doi:10.1016/j.aca.2014.05.042.
[30] S.F. Patil and S.T. Lonkar, J. Chromatogr. A 684, 133 (1994). doi:10.1016/S0021-9673(94)89139-7.
[31] R.R. Arnts, Atmos. Environ. 44, 1579 (2010). doi:10.1016/j.atmosenv.2010.01.004.
[32] M. Dechow, H. Sohn and J. Steinhanses, Chemosphere 35, 21 (1997). doi:10.1016/S0045-6535(97)00135-5.
[33] K.-H. Kim and H.T. Nguyen, J. Sep. Sci. 30, 367 (2007). doi:10.1002/jssc.200600352.
[34] Y.-H. Kim and K.-H. Kim, Anal. Chem. 84, 8284 (2012). doi:10.1021/ac301792x.