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AUTOMATED THERMAL DESORPTION TUBE SPIKING OF VOLATILE ORGANIC COMPOUNDS (VOCS) USING GERSTEL DYNAMIC HEADSPACE SAMPLER

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INTRODUCTION

The spiking of standards (internal standards, surrogates and recovery standards) onto Thermal Desorption Tubes is done widely in laboratories which do environmental & occupational exposure testing.

There are currently two main approaches:

- Spiking with Gas Standards (manual or automated)
- Manual tube spiking with liquid solutions directly onto the sorbent

Spiking with gas standards is relatively easy to automate using valves and mass flow controllers but, requires a gas standards generator or the purchasing of standards in canisters. Both options have a significant cost and spiking reactive species (e.g., carbonyls) and semi-volatiles can be challenging or impossible.

Liquid tube spiking overcomes the issues in the range of analytes that can be spiked onto tubes but, the standards are spiked onto the tubes in the liquid phase whilst the analytes are sampled in the gas phase; this can lead to systematic bias. Furthermore, manual tube spiking is time consuming, labour intensive, imprecise and error prone.

Whilst the GERSTEL Tube Spiking System (TSS) eliminates human error and is a proven, effective, and established solution for the precise, automated spiking of liquid samples directly onto thermal desorption tube; it has limited capacity and does not resolve the potential for bias.

There is clearly a need for a robust, reliable and cost-effective solution that combines the advantages of liquid and gas phase tube spiking.

The GERSTEL Dynamic HeadSpace (DHS) Sampler is a trusted method for extracting liquid phase samples onto thermal thermal desorption tubes providing large enrichment factors which is useful for low level compounds for a multitude of matrices.

We therefore evaluated the GERSTEL Dynamic Headspace (DHS) Option as a novel, high-capacity, tube spiking solution and compared its performance to the GERSTEL Tube Spiking System (TSS).

INSTRUMENTATION

Dual head MultiPurposeSampler Robotic (MPS Robotic)
GERSTEL Dynamic Headspace Sampler 3.5+ (DHS 3.5+)
GERSTEL Tube Spiking System (TSS)
GERSTEL Thermal Desorber (TD3.5+)
GERSTEL Cooled Inlet System (CIS 4C)
GERSTEL Universal Peltier Cooler (UPCPlus)
Agilent GC 7890B coupled to Agilent 7250 Q-TOF MS, Low energy EI source.
Tenax CIS liner

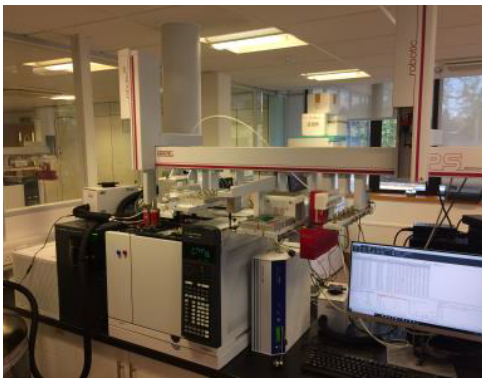

Figure 1: GERSTEL Dual Head Robotic MPS on top of Agilent GC/Q-TOF

METHOD

The GERSTEL TSS was used to spike Carbotrap300 thermal desorption tubes. 1 µL (1 µg/mL) Restek VOC mix was spiked onto each tube (equating to 1 ng of each compound per tube). These were desorbed using the GERSTEL TD3.5+ and CIS 4C combination utilising liquid nitrogen as cooling to achieve a cold trap temperature of -30°C on the CIS (Cooled Injection System).

The GERSTEL DHS 3.5+ option was used to spike a further ten tubes, loading liquid standards into the DHS module and transferring the analytes and solvent, in the gas phase onto standard 3.5 x ¼" Thermal Desorption tubes with the GERSTEL Fully Evaporative Technique (FET).

1 µL of the Restek VOC solution was spiked into 10 mL vials which were transferred onto the same tubes by DHS:

- Incubation temperature: 50°C for five minutes
- Flush volume: 1 L, 100 mL/min
- Trap temperature: 25°C

Tubes were desorbed and analysed using the same TD3.5+ and CIS method as for those directly spiked using the TSS.

Click on Figure 1, for a video that demonstrates the DHS in action.

RESULTS

Relative standard deviations (RSDs) were calculated for both sets of results from the tube Spiking System (TSS) and DHS methods 1 ng loading per tube.

Average peak areas were compared between the two sets of data to obtain a percentage recovery for the DHS method assuming 100% recovery from tubes loaded using the TSS.

Table 1 displays this data for all compounds analysed.

Table 1: RSD values for all eleven compounds.

Compound	TSS %RSD n=10	DHS %RSD* n=9
(Z) 1,2-dichloroethene	3.4	4.73
(E) 1,2-dichloroethene	1.64	6.09
1,2-dichloropropene	2.47	5.85
1,2-dichlorobenzene	2.24	5.71
Tetrachloroethylene	2.03	6.14
Chlorobenzene	2.13	5.06
Ethylbenzene	2.03	4.76
m/p-Xylene	2.33	4.86
o-Xylene	1.89	7.62
Styrene	2.99	7.94
Toluene **	14.2	15.91

*one replicate removed from DHS data due to an outlier **Toluene reproducibility affected by a high background

The DHS produces very good data being outperformed slightly by the TSS. This is perhaps not surprising since the TSS produces highly reproducible data (as outlined in previous application notes AS201 and AS203) and, as a dedicated tube spiking option has undergone extensive optimisation. The DHS spiking used default FET parameters and experimental optimisation using Design of Experiments would likely improve the precision.

Due to the location of our laboratory (next to the A14) we have a high background of Toluene in our laboratory air: this is likely responsible for the much higher standard deviations observed for this analyte.

Table 2 shows the recoveries from tubes spiked using the DHS in comparison to TSS loaded tubes, assuming 100% recovery of 1 ng from those tubes prepared by the latter method. Recoveries all within 75% to 125%. Toluene producing the highest recovery at 120.50% due to background levels present.

Table 2: DHS tube spiking recoveries assuming 100% recovery using the TSS

Compound	Average recovered amount, ng	DHS %RSD* n=9
(Z) 1,2-dichloroethene	1.15	114.66
(E) 1,2-dichloroethene	0.98	97.51
1,2-dichloropropene	0.98	97.56
Tetrachloroethylene	0.91	91.04
Chlorobenzene	0.88	87.67
Ethylbenzene	1.01	101.07
m/p-Xylene	1.07	107.27
o-Xylene	1.02	102.48
Styrene	1.17	116.93
1,2-dichlorobenzene	0.87	86.83
Toluene	1.21	120.50

Spiking tubes by both TSS and DHS produces very similar chromatographic results. Figure 2 displays the chromatogram produced from both methods using combined extracted ion chromatograms for each compound.

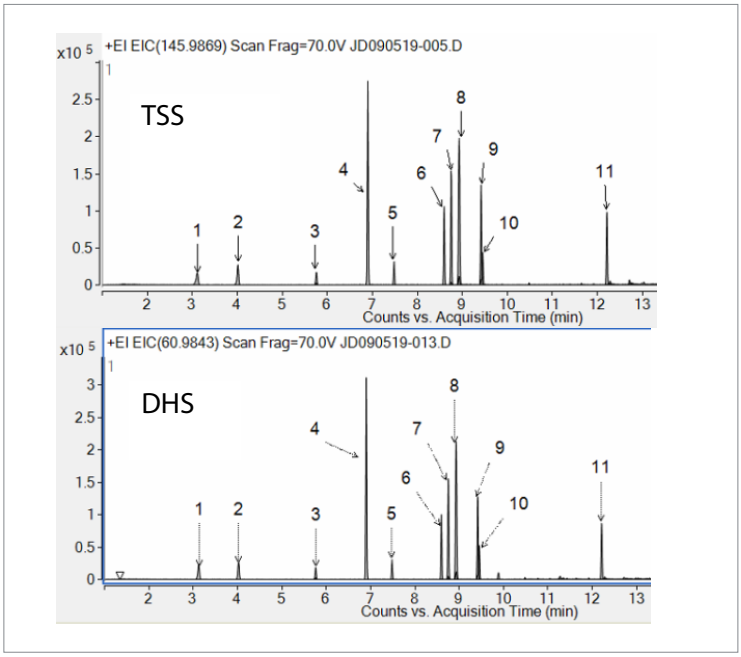

Figure 2: Comparative chromatogram between the two methods of tube spiking: 1 - (Z) 1,2-dichloroethene, 2- (E) 1,2-dichloroethene, 3 - 1,2-dichloropropene, 4 – Toluene, 5 - 1,2-dichlorobenzene, 6 - Tetrachloroethylene, 7 – Chlorobenzene, 8 – Ethylbenzene, 9 - m/p-Xylene, 10 - o-Xylene, 11 - Styrene

DISCUSSION

Using the TSS to spike thermal desorption tubes delivers highly repeatable results when compared to manual spiking, virtually eliminates the potential for human error (mis-/double spiking) and allows tubes to be spiked in batches of 30 (max. 2 banks of 3 x 5 samples).

By comparison, using the DHS module for Fully Evaporative Tube Spiking potentially allows up to 960 tubes to be spiked (2 m MPS Rail) in full automation, either on a standalone DHS Tube Spiking Prepstation or integrated online with any Agilent GC/GC-MS.

Where standards are being applied immediately before desorption, spiking and analysis of the TD tube is fully automated with minimal analyst intervention: the only manual requirement being to load the tubes and vials into a rack.

This brings the further advantage of preparing large amounts of tubes overnight and during the course of a weekend which can increase throughput. It is worth nothing that this method of tube loading was not optimised and times could potentially be shortened to further improve cycle time and throughput.

Figure 3 shows the PrepSequence timeline using the DHS.

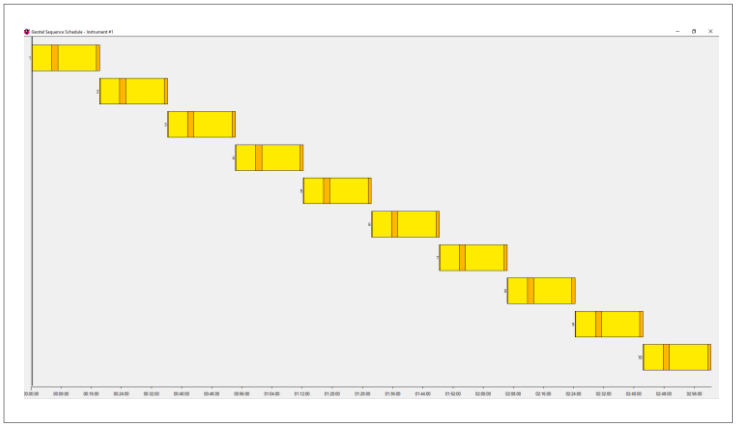

Figure 3: PrepSequence timeline of TD tube spiking using the DHS. As the DHS is being utilised for an offline solution, there is no GC injection.

Employing this methodology results in ten tubes prepared in three hours, which when multiplied up to a full rack of forty tubes, takes twelve hours. This can be carried out overnight so that preparation is complete by morning. Having more TD racks available means extra capacity over the weekend. A minimum weekly throughput of 200 tubes can be prepared. To minimise the risk of analyte loss through evaporation of the standard solution, a Peltier cooled stack may be used. This is a big advantage to those who need to greatly increase production of pre-spiked tubes.

Using the GERSTEL Dynamic Headspace (DHS 3.5+) for tube spiking is a viable alternative to both manual tube spiking and using the GERSTEL Tube Spiking System (TSS).

Initial results demonstrate better precision than manual tube spiking.

Further optimization using Design of Experiments is required to increase throughput and deliver equivalent precision to Tube Spiking using the GERSTEL TSS.

The ability for high capacity tube spiking with the DHS system means that a dedicated offline PrepStation can be used to spike tubes for multiple dedicated TD-GC/MS systems (e.g., new GERSTEL MultiPurpose Sampler TD3.5+).

Using the DHS to fully automate tube spiking (including calibration standard spiking) virtually eliminates labour costs and the potential for human error.

Combining the GERSTEL Dynamic Headspace option with other GERSTEL MultiPurpose Sampler options:

Automated preparation of calibration standards
Tube spiking from non-volatile matrices
GERSTEL SID Barcode Reader
GERSTEL Sequence by Barcode

Combining the GERSTEL Dynamic Headspace option with TSS Manager for a single solution for Gas and Liquid phase tube spiking.

If you would like further information about Tube Spiking using either the GERSTEL Tube Spiking System or GERSTEL Dynamic Headspace option, please contact Anatune by e-mail: enquiries@anatune.co.uk or Telephone: 01223 279210.