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Automated Solution for Spiking Thermal Desorption Tubes using GERSTEL Tube Spiking System and TD3.5+

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Introduction

Anatune recently added the GERSTEL Tube Spiking System (TSS) to its toolkit to compliment the already varied techniques available in thermal desorption (TD). The TSS gives the MPS the capability to liquid spike TD tubes covering the size range of 60mm, 89mm (3.5 inch) and 178mm in length. As a result, tubes covering a wide range of applications can be prepared and analysed by a wide range of analysers.
The availability of this option has enabled Anatune to collaborate with Health and Safety Laboratory (HSL) to automate the spiking of TD tubes.
In particular, HSL expressed an interest in automating their current method of hand spiking semi-volatile organic compounds (SVOCs) on to TD tubes. The main benefits of automation precision and accuracy, health and safety and, when compared with hand spiking, time efficiency savings.
For the work they carry out, HSL require tubes loaded with a precision of better than 2% and, ideally, close to 1%. Consequently, any new automated procedure needs to able to at least match this level of precision.

The aim of this work was to demonstrate the feasibility and MPS capabilities of liquid spiking VOCs onto 3.5 inch TD tubes for quantitative analysis at HSL on their TD-GC-FID and also analysis at Anatune using GERSTEL's TD3.5+ thermal desorption unit.

Here is an example of the Tube Spiking System which is attached to the MPS rail with TD tubes. **For a demonstration of the Tube Spiking System at work [click here](#).**

Instrumentation

GERSTEL MPS Robotic Dual head Robotic/Robotic^{Pro}
GERSTEL Tube Spiking System
Agilent 7890GC/7010QQQ
GERSTEL TD3.5+
GERSTEL CCD2
GERSTEL CIS 4
Masshunter B.07

Method

3.5 inch Tenax TD tubes, supplied by Health and Safety Laboratory (HSL) were placed in each of the TSS positions. Each tube was spiked with 5 µL of a known standard using the Robotic^{Pro} equipped with Universal Syringe Module and a 10 µL syringe. The components in the test standard were volatile organic compounds (VOCs) rather than SVOCs. This is because the objective of this test was to test the reproducibility (precision) of the automated liquid loading system with components directly comparable to those currently used at HSL. Half of the spiked tubes were sent back to HSL for analysis with the remaining half left for analysis on the GERSTEL TD3.5+.
Ten replicates were spiked with a stock of low concentration giving an approximate loading of 25 ng per tube. This was repeated with another set of ten tubes spiked with another solution to give a loading of 200 ng. One blank tube was analysed alongside each set of replicates.

A calibration curve was also prepared by spiking 1 µL, 2.5 µL, 5 µL and 7.5 µL of one solution to test linearity but was not used in for quantitation. The tubes were left to flush with nitrogen gas for 30mins to remove any residual solvent.

Transport adapters were applied to each tube and loaded onto TD3.5+ sample tray and analysed using the GERSTEL MPS Robotic to automate the analysis. The TD3.5+ was set to splitless mode with the CIS 4 in solvent vent settings using the inlet purge flow to set a split flow of 120:1 Samples were analysed using a DB-5 column which was of similar phase to that being used by the customer, with the Mass spec. running in SIM mode.
For temperatures, TD transfer temperature was set at 280°C, with a desorption temperature of 30°C up to 250°C. During desorption, the CIS 4 was kept was at -30°C then later ramped up 250°C. A CIS 4 Tenax TDU liner was used to aid trapping of the compounds in the inlet during desorption. For cooling, a GERSTEL CCD2 2-channel cryostatic cooling device was used.

Results

Agilent Masshunter B.07 Quant was used to assess the data, using p-xylene as internal standard for quantification using a one point calibration. A typical chromatogram of a 25ng standard and a blank can be seen below in figure 2.

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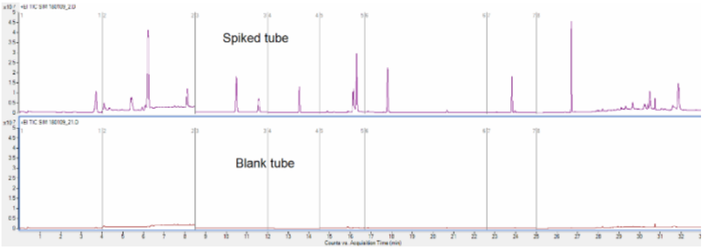

Figure 1. Chromatogram of a spiked tube compared with a blank

The data for two compounds, methyl isobutyl ketone and limonene along with %RSD is displayed for both the low and high spikes.

Tube no.	Calculated concentration(ng)
1	25.1
2	24.3
3	24.9
4	24.5
5	25.8
6	24.2
7	24.7
8	24.9
9	24.2
%RSD	2.08

Table 1 – methyl isobutyl ketone 25ng

Tube no.	Calculated concentration(ng)
1	187
2	193
3	196
4	191
5	183
6	178
7	186
8	187
9	183
%RSD	2.91

Table 2 – methyl isobutyl ketone 200ng

Tube no.	Calculated concentration(ng)
1	24.0
2	24.1
3	24.1
4	24.6
5	24.7
6	23.1
7	24.2
8	23.8
9	23.9
%RSD	1.96

Table 3 – limonene 25ng

Tube no.	Calculated concentration(ng)
1	196
2	203
3	209
4	206
5	201
6	216
7	207
8	208
9	207
%RSD	2.73

Table 4 – limonene 200ng

Linearities as described below in Table 5 all greater than 0.995

Compound	Retention Time (min)	R^2
Benzene	3.66	0.9981
Methyl isobutyl ketone	5.36	0.9962
Toluene	6.17	0.9971
Butyl acetate	8.08	0.9981
p-xylene	10.48	0.9999
Cyclohexanone	11.54	0.9999
α-pinene	13.52	0.9999
Phenol	16.15	0.9966
1,2,4-trimethylbenzene	16.30	0.9998
Limonene	17.80	0.9976
Dodecane	23.82	0.9999
Phenyl cyclohexene	26.69	0.9996

Table 5 – R^2 values for all compounds analysed

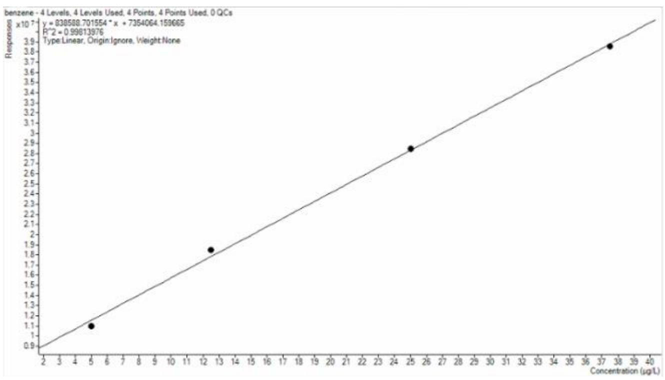

Figure 2. Benzene R^2-0.9981

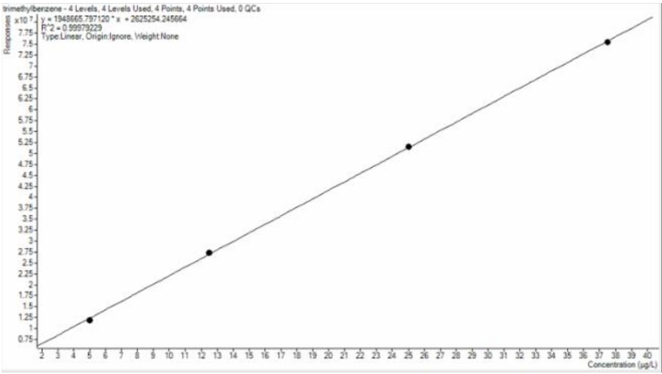

Figure 3. 1,2,4-trimethylbenzene R^2-0.9998

Duplicate TD tubes were sent to the customer's laboratory for analysis using a TD coupled to a GC-FID system. The %RSD data from ten tubes loaded with 25ng per analyte can be seen in the below table. The data shows good reproducibility across the full suite of compounds showing that this application is suitable for these types of compounds.

Compound	%RSD
Benzene	2.53
Methyl isobutyl ketone	0.62
Toluene	1.64
Butyl acetate	5.33
p-xylene	2.41
Cyclohexanone	1.36
α-pinene	0.71
Phenol	2.65
1,2,4-trimethylbenzene	1.01
Limonene	1.03
Dodecane	1.06
Phenyl cyclohexene	4.00

Table 6 - %RSD for duplicate tubes at 25ng

Discussion

Automated spiking of thermal desorption tubes is now possible using a GERSTEL MPS. Multiple Tube Spiking System may also be used to increase throughput whilst maintaining precision.
Using a GERSTEL MPS to spike TD tubes enables the user to spike tubes at varying concentrations simultaneously and precisely.
Compounds that were previously spiked on TD tubes using an air-loading setup can be spiked in liquid form.
The method used to spike the TD tubes was not optimized for injection depth and the time spent flushing with nitrogen after spiking, but the data shows the method used was reproducible.
A recovery exercise to assess absolute loading was not carried out. Further work will be done to assess the suitability of spiking tubes with semi-volatile compounds (SVOCs).

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