

AUTOMATED SIFT-MS: STATIC HEADSPACE ANALYSIS

Mark Perkins, Anatune Ltd., Girton, Cambridgeshire (UK).

INTRODUCTION

Traditionally, analysis with SIFT-MS has relied on either passive ambient monitoring or manual introduction of large volume gas or headspace samples. In previous Application Notes (AS191, AS209 and AS212) it has been shown that by combining the power of direct analysis using Selected Ion Flow Tube Mass Spectrometry and GERSTEL automation (automated SIFT-MS), headspace analysis of volatile compounds can be greatly simplified. Additionally, with analysis time allowing for at least 15 samples per hour to be run, significant gains in sample throughput can be achieved.

Recently, a series of webinars have been broadcast looking at a wide range of automated SIFT-MS applications and methods. This application note is intended as a useful starting point for the development of static headspace methods using automated SIFT-MS and the information builds on a significant amount of method development, carried out in the Anatune Applications Laboratory, and should serve as a best-practice for these types of analyses.

INSTRUMENTATION

SIFT-MS: Syft Technologies Dual Polarity Voice200*ultra* with GERSTEL MPS Robotic Pro autosampler.



Figure 1: Syft Technologies Voice200*ultra* SIFT-MS with GERSTEL MPS Robotic autosampler.

Details of the SIFT-MS technique can be found in Application Note AS191.

To enable measurements to be made using SIFT-MS, the analytes have to be in the gas phase, therefore, automated SIFT-MS relies on headspace analysis. Additionally, SIFT-MS requires the analytes to be injected over an extended period of time (from 10 seconds up to 2 minutes, or longer) to enable concentrations to be calculated. However, unlike GC-MS, the injection time is also the measurement time. Consequently, GERSTEL MPSr syringe-based approach offers the slow

injection control needed. Figure 2 shows a schematic difference between the two techniques.

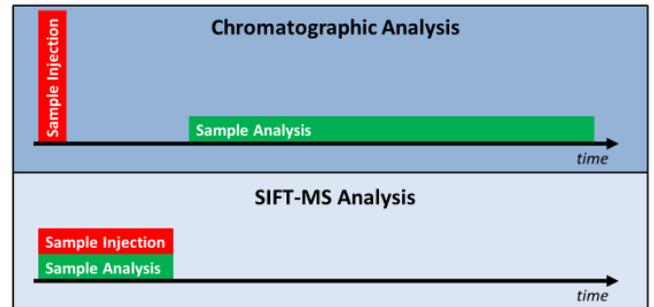


Figure 2: Example static headspace injection.

Figures 3 and 4 show an example static headspace injection on an automated SIFT-MS, showing the portion of the injection phase that is used for the concentration calculation.

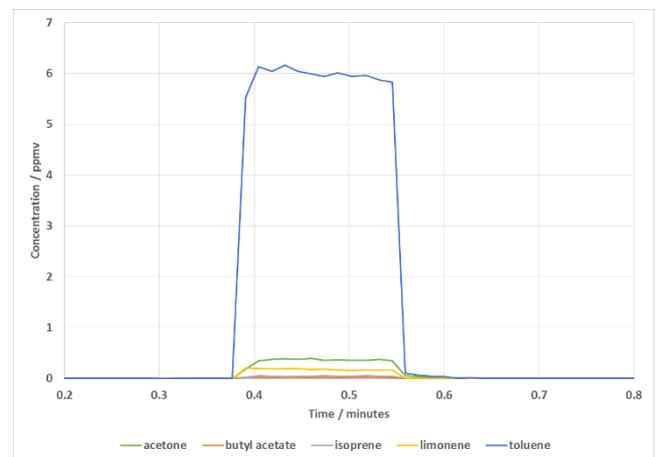


Figure 3: Example static headspace injection.

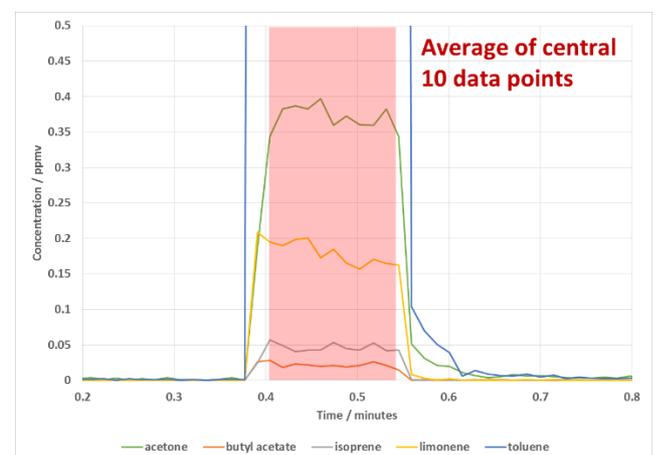


Figure 4: Example static headspace injection showing region used for concentration measurements.

Currently, static headspace injection sequences are generated using PrepSequences in GERSTEL's Maestro software and Figure 5 shows a typical PrepSequence used for static headspace analysis. The remainder of this Application Note will describe the various parts of the PrepSequence, and range of parameters used.

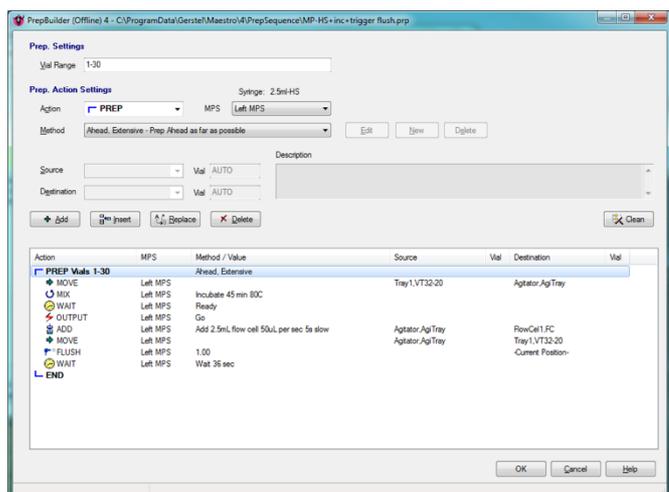


Figure 5: Typical PrepSequence used for static headspace analysis.

METHOD

As shown in Figure 5, there are a number of steps required to carry out an incubated, static headspace analysis.

Vial Range: This defines the number, and range of vials to be analysed.

Mix: This defines the incubation parameters. A method dialogue box allows the incubation length, incubation temperature and mixing speed to be set. As this method uses PrepSequences, a specific **Move** command is required to move the vials to and from the Agitator.

Wait and Output: These commands allow the GERSTEL MPSr to trigger the required method on the SIFT-MS.

Flush: Allows for the headspace syringe to be flushed with clean gas, post-injection. Depending on the volatility of the species being analysed, the flush time can vary from 30 seconds to 3 minutes for effective syringe cleaning.

Wait: The final wait command is used to optimise extended sequences and will be discussed later in this Application Note.

Add: The Add command is used to inject the headspace sample, via the heated headspace syringe, into the SIFT-MS inlet. As with all sample introduction, the parameter used will have a direct impact on the quality of results obtained. Figure 6 shows the dialogue box where these parameters are set.

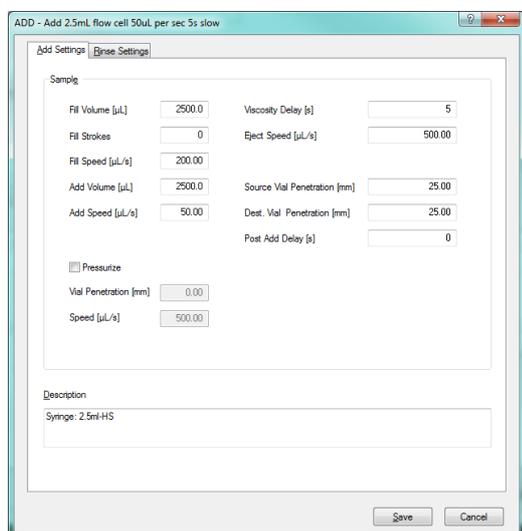


Figure 6: Add command dialogue box.

Add Volume and **Add Speed** are used to define how long the sample will be introduced to the SIFT-MS for. The SIFT-MS inlet has a fixed flow rate of approximately 25 mL/min (varies between instruments). For example, a 2.5 mL headspace injection at 50 $\mu\text{L}/\text{sec}$ equates to a 50 second injection at 3 mL/minutes. For this reason, a make-up flow of 22 mL/minute needs to be added to bring the total flow to 25 mL/minute. Figure 7 shows the dilution effect of injection speed on the measured concentration. This dilution has the effect of reducing the concentration measured by the instrument and consequently, the sensitivity of the method. However, it does increase the number of data points across the injection, leading to greater accuracy of measurement. It is recommended that at least 8 data points should be measured across the injection phase. For this reason, injection speeds of between 25 to 100 $\mu\text{L}/\text{sec}$ is a good compromise between sensitivity and accuracy.

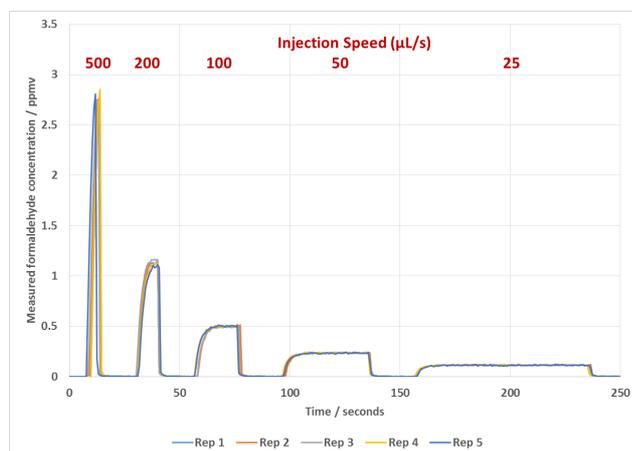


Figure 7: Example of variable injection speeds and the effects on measured concentration.

Appendix A in Application Note AS191 describes a temperature correction factor that also needs to be applied to the measured concentrations, to correct for any temperature difference between the headspace syringe and the incubation temperature. To summarise, the correction factor is generated by dividing the temperature of the headspace syringe, in Kelvin, by the incubation temperature, in Kelvin, of the headspace vial.

Therefore, to obtain accurate headspace concentrations, these two correction factors need to be applied to the instrument measured concentrations. Figure 8 shows an example calculation for a typical set of incubation and injection parameters and Figure 9 shows each correction factors contribution.

Need to apply dilution multiplier to get correct concentrations.

- Injection / flow rate correction
- Incubation / syringe temperature correction

Injection speed = 50 $\mu\text{L}/\text{sec}$ (3 mL/min)
 Inlet flow = 25 mL/min
 Incubation temperature = 60°C (333K)
 Syringe temperature = 150°C (423K)

$$\text{Dilution multiplier} = (25 \div 3) \times (423 \div 333) = 10.6$$

Figure 8: Typical correction factors for measured headspace concentration.

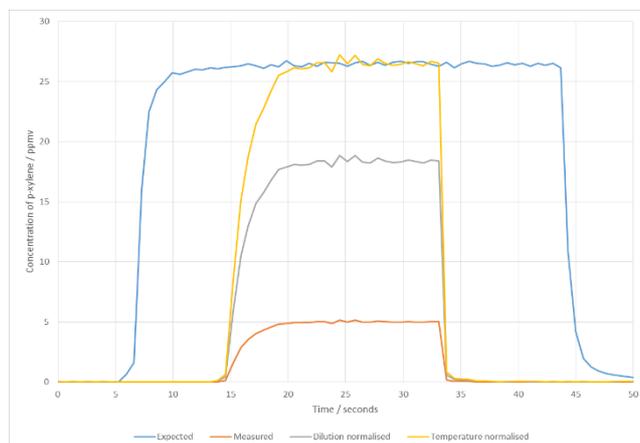


Figure 9: Result of applying dilution multipliers to obtain the correct headspace

concentration.

It should be noted that, if a set of calibration standards are run prior to samples being analysed, and all test conditions are identical, then it is not necessary to apply the correction factors, as concentrations can be calculated from the calibration set. Application Notes AS209 and AS212 are examples of this approach.

Viscosity Delay: This sets the length of time the syringe plunger will be held at the end of its fill phase, to allow for equilibration of the vapour within the syringe barrel. Figure 10 shows the effect of extending this from 0 to 5 seconds and it can be seen that at short delay times a significant under-reporting of the concentration can occur. It is suggested that 5 seconds is an effective delay for most volatile compounds. **Fill Speed** should also be considered, as faster fill speeds will require longer viscosity delays and fill speeds of around 200 µL/sec have been shown to be suitable.

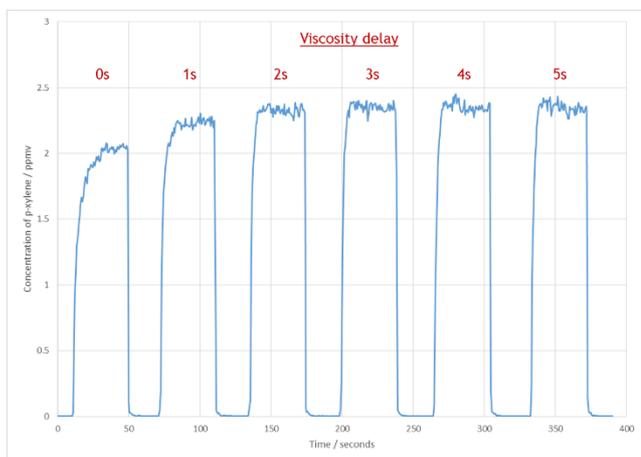


Figure 10: Example of variable viscosity delay on measured concentration.

Wait: The PrepSequence shown in figure has a Wait command of 36 seconds as the last step in the sequence. The purpose of this command to optimise the scheduling of the incubations and injections into the SIFT-MS.

As shown in Figure 2, the lack of chromatographic separation for SIFT-MS measurements means that the sample introduction time *is* the sample measurement time, and this significantly reduces the method runtime. Unlike GC-MS methods, where the rate limiting step for a static headspace method is often the GC-MS runtime, the short sample measurement time for SIFT-MS methods leads to the incubation time always being the rate limiting step. This is shown graphically in Figure 11.

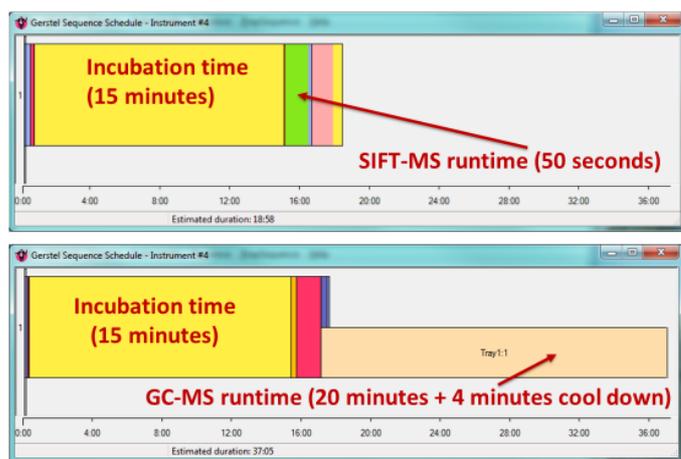


Figure 11: Example incubation and injection sequence for SIFT-MS and GC-MS analysis (shown on same time axis to demonstrate the difference in runtime for each technique).

The standard Agitator on the GERSTEL MPSr system has 6 positions (although this can be increased to 12 if required) and these will start to be filled as the PrepAhead function of the Maestro software optimises the sequence. Once the first incubation is completed, the system will start the injection phase of the sequence, and again, this is optimised by the PrepAhead function. One consequence of this is that method does not include any time to remove the tested vial from the Agitator and to add a new one to the sequence. This can be seen in Figure 12,

where the first five vials in the sequence of eight are all analysed before being moved and this leads to the “dog-leg” effect in the sequence. This is very rarely seen with GC-MS methods where there is time within the method to move the analysed vial out of the Agitator.

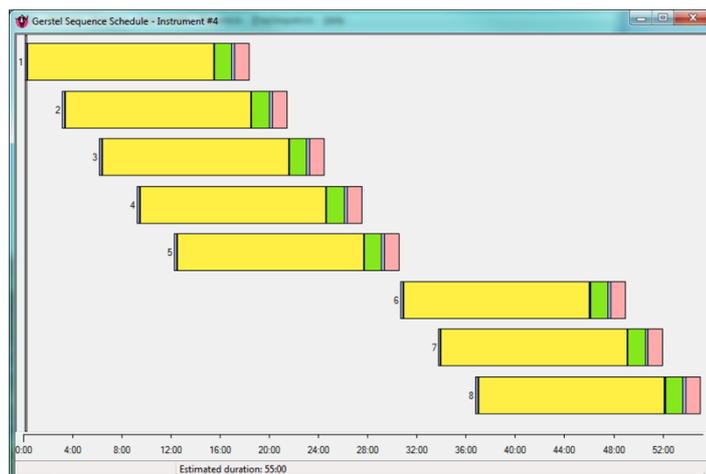


Figure 12: Example of inefficient scheduling of a static headspace sequence with automated SIFT-MS.

Figure 13 shows that by adding a short Wait statement after the end of the analysis, there is now time to move vials in and out of the empty Agitator positions, leading to a significantly more optimised sequence – in this case shortening the overall runtime by 20%.

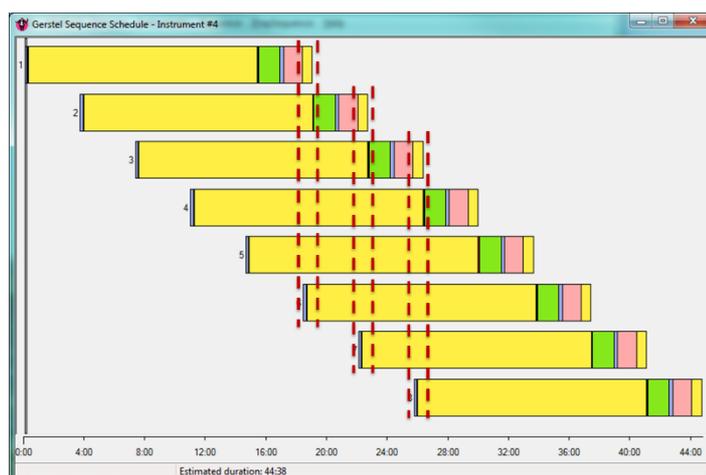


Figure 13: Effect of using a short “Wait” command at end of injection phase.

DISCUSSION

Automated SIFT-MS has been shown to offer significant throughput gains for a number of different headspace analysis techniques, as well as simplifying the overall analytical methodology. However, due to the differing requirements of SIFT-MS when compared to GC-MS, principally around the injection part of the analysis, the parameters used will differ to those usually seen for HS-GC-MS. From the extensive method development carried out in Anatune’s Applications Laboratory we have been able to determine a suitable range of parameters to be used, and these have been detailed in this Application Note. It should be noted that these should not be treated as definitive, as applications will have differing needs related to the analyte suite, but they do offer a very good starting point for subsequent method development.

REFERENCES

- [AS191 – Automated Selected Ion Flow Tube Mass Spectrometry \(SIFT-MS\)](#)
- [AS209 – Rapid Analysis of BTEX in Water Using Automated SIFT-MS](#)
- [AS212 – Rapid Analysis of Organochlorine Compounds in Water Using Automated SIFT-MS](#)