

## Automated Spiking of Internal Standards and Surrogates using the GERSTEL MPS Prepstation

*Jonathan Angove, Anatune Ltd., Hardwick, Cambridgeshire, UK.  
Keith Summerhill, Anatune Ltd., Hardwick, Cambridgeshire, UK.*

### Introduction

Automating the addition of internal standards and surrogates enables accurate and reproducible volumes to be added to each vial in a just-in-time manner prior to injecting the sample.

By proving this application by spiking internal standards and surrogates for VOC analysis in water, the reproducibility achieved with less volatile components should be at least as good over a similar timescale. By using the Anatune 160 position tray, 160 samples were spiked with internal standards and surrogates prior to their on-line analysis, taking approximately 27 hours.

A 2.5mL gastight syringe was used for headspace sampling and a 25µL liquid syringe was used for spiking the internal standards and surrogates. As a result, it was necessary to use the MPS Prepstation variant. When performing liquid sampling, whether for LC or GC analysis, if the injection volume and internal standard/surrogate volumes are compatible with a single syringe, then a single rail MPS 2 may be used.

The GERSTEL Maestro software was used to control both MPS rails and was used to write the sample preparation sequence. This software can be integrated into ChemStation, so a single prep-sequence can be used to both add internal standards and surrogates and to perform the sample injection. This prevents any possible transcription errors that can occur if several sequences need to be written and synchronised to perform the analysis.

### Instrumentation and Methods

- GERSTEL MPS Prepstation, one rail configured for headspace analysis, the second rail for liquid addition
- Agilent 6890N Gas Chromatograph with 5975B inert MSD
- GERSTEL Maestro software
- Agilent ChemStation
- Anatune 160 position tray
- Anatune CoolR+
- Anatune OptimisedVOC method as detailed in Anatune application note AS30

### Compound List

Internal Standards	Surrogate Compounds
Pentafluorobenzene	1,2-Dichloroethane-d6
Difluorobenzene	Toluene-d8
Chlorobenzene-d5	4-Bromofluorobenzene
1,4-Difluorobenzene	

### Sample Preparation

Aqueous blanks were prepared by weighing anhydrous sodium sulphate into a vial before adding the required volume of water and capping the vials. No further sample handling was required.

### Headspace GC-MS Method

Given the relative simplicity of the sampling procedure, the MPS Prepstation is able to perform the fully automated spiking of internal standards and surrogates before headspace sampling in a high-throughput, “just-in-time” manner. This enables one sample to be running on the GC-MS while further samples are being prepared; the preparation process being completed just after the GC-MS is ready for the next injection to occur. Reliable transport of vials between the sample tray and the heated agitator is achieved by the use of magnetic vial caps.

Figure 1 shows the MPS Prepstation used for this work

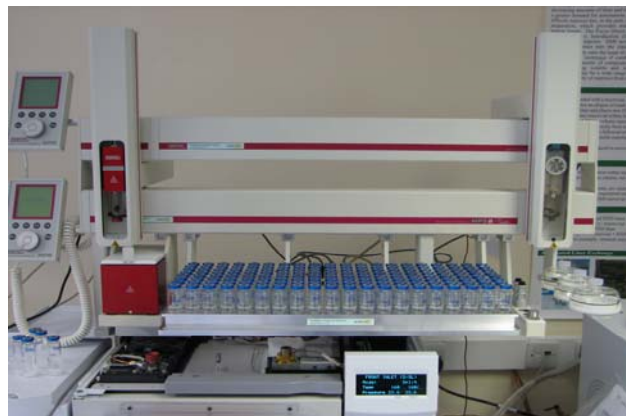


Figure 1



## Results

To meet regulatory criteria for precision and accuracy, the %RSD of the surrogate concentration for a batch of samples must be below 15% and the concentration bias, the difference from the spiked concentration, must be less than 30%. The internal standards and surrogates were spiked at 100µg/L, so a concentration between 70 and 130µg/L meets the regulatory criteria. Figures 2, 3 and 4 show the calculated concentrations of each or the three surrogates previously listed during the course of the analysis of 160 headspace samples.

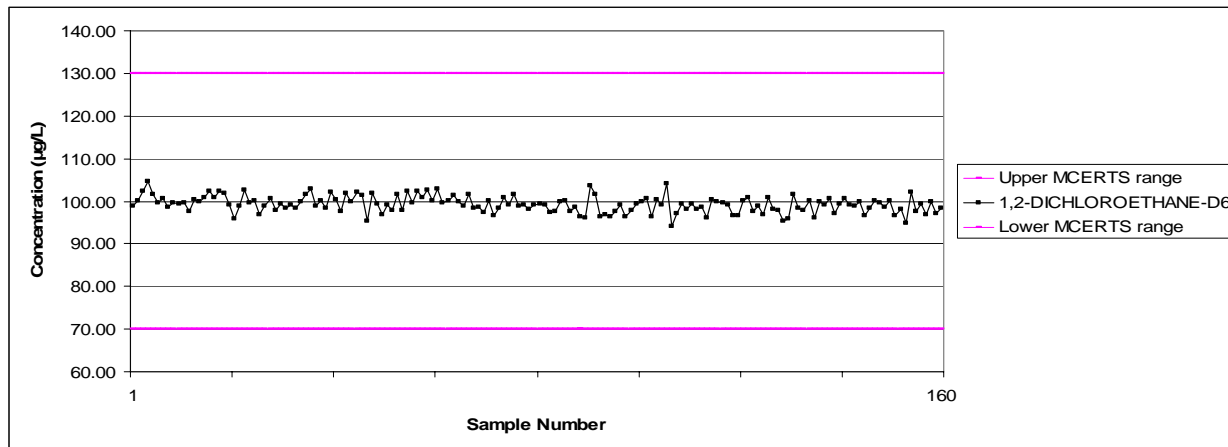


Figure 2

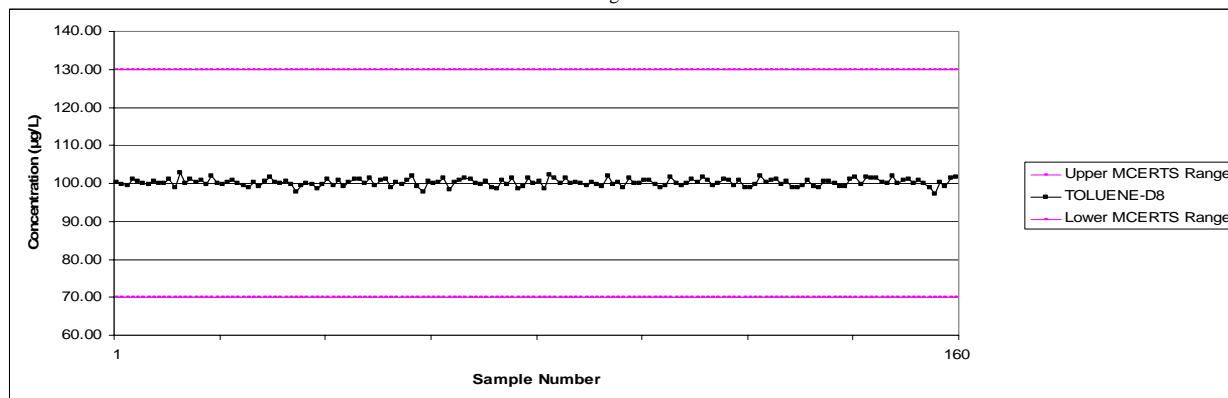


Figure 3

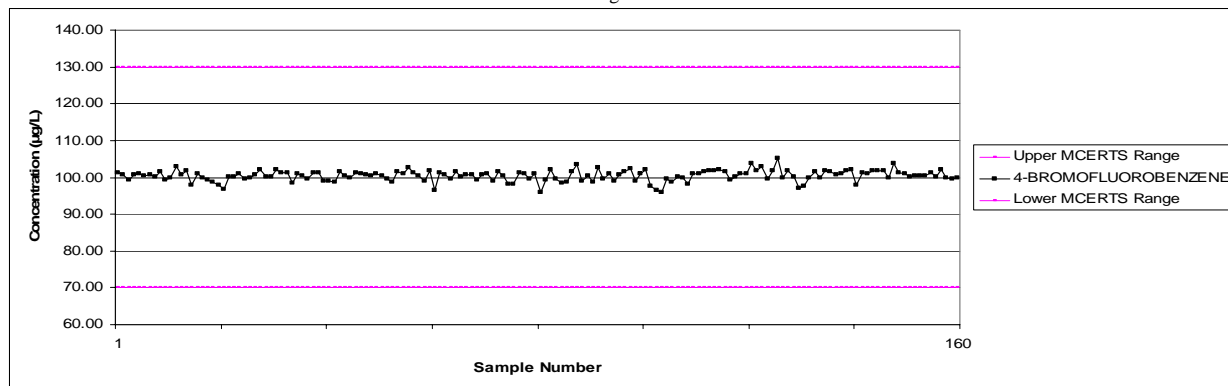


Figure 4



The mean abundance and %RSD figures for each internal standard from the entire batch of 160 samples are listed below.

<b>Internal Standard</b>	<b>Mean</b>	<b>% RSD</b>
Pentafluorobenzene	690638.73	6.63
Difluorobenzene	1089288.09	6.67
Chlorobenzene-d5	462925.03	6.85
1,4-Dichlorobenzene-d4	500771.92	6.51

The mean concentration, %RSD and bias figures for each surrogate from the entire batch of 160 samples spiked at 100µg/L are listed below.

<b>Surrogate Compounds</b>	<b>Mean</b>	<b>% RSD</b>	<b>Bias (%)</b>
1,2-Dichloroethane-d6	99.25	1.97	-0.75
Toluene-d8	100.21	0.96	+0.21
4-Bromofluorobenzene	100.42	1.50	+0.42

### ***Conclusions***

---

The spiking of volatile internal standards and surrogates represent the most technically challenging group of compounds, due to the ease with which evaporative losses can occur. This work demonstrates that even in this context, the automation of standard addition is a practical proposition, and can be used to save both skilled analyst's valuable time and further reduce the opportunity for human error in the analytical process.