



Chromatography Technical Note No AS59

On-line Construction of Calibration Curves for the Analysis of Selected Red-list Solvents & THMs in Water using the GERSTEL MPS Prepstation

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Introduction

This note follows on from Anatune application notes AS30, AS45, AS53, AS55, AS56 and AS 58 and extends that work by automating the addition of solutions of standards, internal standards and surrogates to calibration and analytical samples for trace analyses. At the beginning of the prep-sequence the MPS Prepstation added an appropriate volume of standard solution to each of the calibration vials. The internal standards and surrogate solutions were subsequently added to the required vials in a “just-in-time” manner. This enables accurate and reproducible volumes to be added to each vial prior to injecting the sample.

20 samples were manually spiked at the 5µg/L level. The MPS Prepstation was used to spike internal standard into these vials in a “just-in-time” manner and also to spike the relevant volumes of mixed standard and internal standard into the calibration sample vials to construct a calibration curve between 0.21 and 20µg/L for each analyte.

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 standards, internal standards and surrogates and to perform the sample injection in a “just-in-time” manner. This prevents any possible transcription errors that can occur if several sequences need to be written and synchronised to perform the analysis.

As detailed in Anatune application note AS58, spiking the mixed standard solution at the beginning of the prep-sequence enabled the Maestro software to prep-ahead the incubation of the calibration samples to maximise the efficiency of the sample analysis.

Instrumentation and Methods

- GERSTEL MPS Prepstation, one rail configured for headspace analysis, the second rail for liquid addition.
- Agilent 6890N GC with 5975B inert MSD.
- GERSTEL Maestro software.
- Agilent ChemStation.
- Anatune 160 position tray.
- Anatune CoolR+.
- Anatune OptimisedRedlist method as detailed in Anatune application note AS33.
- The automated spiking of standards to construct calibration curves as detailed in Anatune application note AS45.
- The automated spiking of internal standards and surrogates into water samples and calibration samples as detailed in Anatune application notes AS53 and AS55.
- The automated construction of on-line calibration curves as detailed in Anatune application notes AS56 and AS58.

Compound List

Internal Standards	
4-Bromofluorobenzene	
Analytes	
Chloroform	Bromochloromethane
1,1,1-Trichloroethane	1,2-Dichloroethane
Benzene	Trichloroethene
Toluene	Carbon tetrachloride
Tetrachloroethene	Dibromochloromethane
m,p-Xylene	o-Xylene
Bromoform	1,3-Dichlorobenzene
1,4-Dichlorobenzene	1,2-Dichlorobenzene
1,2,4-Trichlorobenzene	Hexachlorobutadiene
1,2,3-Trichlorobenzene	

Sample Preparation

Anhydrous sodium sulphate was weighed into 27 vials before adding the required volume of water. The vials to be used to construct the calibration curve were capped and placed on the MPS Prepstation for automated standard and internal standard addition. 20 replicate samples were manually spiked to a concentration of 5µg/L before being capped and placed on the MPS Prepstation for automated internal standard addition.

Headspace GC-MS Method

Each calibration sample was spiked with the appropriate volume of mixed standard at the start of the prep-sequence. Because the prep-ahead function within the Maestro software is limited to those analyses contained within a single "job", sequential spiking of the standard solution into the calibration vials at the beginning of the prep-sequence is a single job. This then allowed the MPS Prepstation to add the solutions of internal standards in a "just-in-time" manner prior to their on-line headspace analysis.

Figure 1 shows the MPS Prepstation used for this work

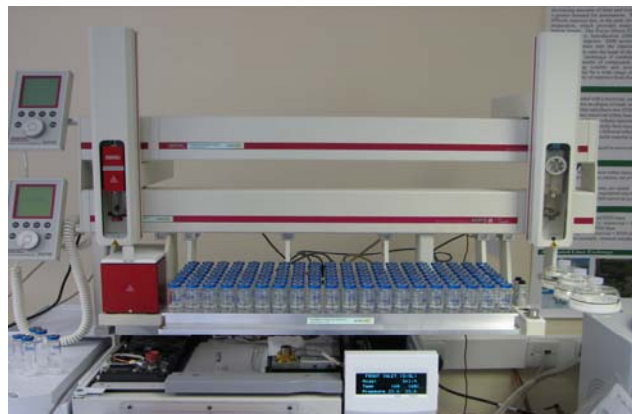


Figure 1

Results

Because this application was performed using a headspace method where the vial incubation time is approximately three times longer than the GC method, spiking the standards into the relevant vials at the beginning of the prep-sequence meant that the internal standards and surrogates and the subsequent headspace analysis was a single "job". This meant that the prep-ahead function within Maestro would, after the initial incubation periods, have subsequent vials spiked and incubated for headspace sampling shortly after the GC came ready for injection.

Table 1 shows the correlation coefficients obtained for each analytes' calibration curve, the mean concentration, standard deviation and relative standard deviation for each analyte.

Internal standard	Mean conc. (n=20)		RSD	%RSD
4-Bromofluorobenzene	274591		31000.82	11.29
Analyte	r ²	Mean conc. (n=20)	RSD	%RSD
Chloroform	1.000	5.27	0.18	3.34
Bromochloromethane	1.000	5.24	0.20	3.80
1,1,1-Trichloroethane	1.000	5.05	0.11	2.28
1,2-Dichloroethane	1.000	5.47	0.32	5.92
Benzene	1.000	5.17	0.16	3.12
Trichloroethene	1.000	5.23	0.20	3.73
Toluene	1.000	5.18	0.12	2.37
Carbon tetrachloride	0.999	5.17	0.17	3.36
Tetrachloroethene	1.000	5.13	0.16	3.10
Dibromochloromethane	1.000	5.34	0.18	3.30
m,p-Xylene	1.000	5.18	0.16	3.01
o-Xylene	1.000	5.23	0.15	2.81
Bromoform	1.000	5.29	0.19	3.56
1,3-Dichlorobenzene	0.999	5.21	0.23	4.33
1,4-Dichlorobenzene	1.000	5.31	0.18	3.45
1,2-Dichlorobenzene	1.000	5.16	0.16	3.08
1,2,4-Trichlorobenzene	1.000	5.27	0.22	4.12
Hexachlorobutadiene	1.000	5.21	0.38	7.37
1,2,3-Trichlorobenzene	1.000	5.32	0.23	4.37

Table 1

Conclusions

This work demonstrates that the automation of the addition of standards and internal standards into both calibration and analytical samples is a practical proposition. The GC-runtime of 5.4 minutes affords sufficient separation of all compounds analysed, significantly increasing laboratory productivity when compared with SIM GC-MS or purge-and-trap methods delivering similar sensitivity whilst reducing the opportunity for human error in the analytical process.