Chromatography Technical Note No AS74

A Summary of the Anatune Environmental VOC System

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Introduction

Headspace sampling for Environmental VOCs is a proven technique for rapid quantitation of soil and water samples and has rapidly become the method of choice for many Environmental testing companies. Anatune has supplied systems for this purpose for many years; the capacity and capabilities of the autosamplers has been enhanced over this time and this application note summarises the options available.

Figure 1 shows the Anatune VOC system with optional capability to automate the addition of internal standard, surrogate and standard solutions.

The headspace sampling was performed by a heated syringe, which was purged with inert gas between samples to reduce carryover between samples. A heated agitator was used to dissolve the salt added to the vials as a matrix modifier and to raise the vial temperature to that set in the method.

The GC runtime for the Anatune VOC method was 5½ minutes. Using the Anatune CoolR^{plus} a cycle time, the time between two subsequent injections, of approximately 8 minutes was achieved.

By designing a large capacity tray holder that is capable of holding up to 240 20mL headspace vials, the GERSTEL MPS 2XL was able to analyse all the samples with only a single time penalty incurred from the incubation time for the first sample.

The addition of a second MPS 2XL to construct an MPS Prepstation facilitates the automated addition of standard, internal standard and surrogate solutions to the vials 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.

Compound List

Internal Standards	**Surrogate Compounds**
Pentafluorobenzene	1,2-Dichloroethane-d6
Difluorobenzene	Toluene-d8
Chlorobenzene-d5	4-Bromofluorobenzene
1,4-Difluorobenzene	
Analytes	
Chloroethane	Bromomethane
Trichlorofluoromethane	1,1-Dichloroethene
trans-1,2-Dichloroethene	1,1-Dichloroethane
cis-1,2-Dichloroethene	Chloroform
Bromochloromethane	1,1,1-Trichloroethane
1,1-Dichloropropene	1,2-Dichloroethane
Benzene	1,2-Dichloropropane
Trichloroethene	Bromodichloromethane
Dibromomethane	cis-1,3-Dichloropropene
Toluene	1,1,2-Trichloroethane
Carbon tetrachloride	1,3-Dichloropropane
Tetrachloroethene	Dibromochloromethane
1,2-Dibromomethane	Chlorobenzene
1,1,1,2-Tetrachloroethane	Ethyl benzene
m,p-Xylene	o-Xylene
Styrene	Bromoform
Isopropylbenzene	1,1,2,2-Tetrachloroethane
1,2,3-Trichloropropane	n-Propylbenzene
Bromobenzene	2-Chlorotoluene
1,3,5-Trimethylbenzene	4-Chlorotoluene
tert-Butylbenzene	1,2,4-Trimethylbenzene
sec-Butylbenzene	p-Isopropyltoluene
1,3-Dichlorobenzene	1,4-Dichlorobenzene
n-Butylbenzene	1,2-Dichlorobenzene
1,2-Dibromo-3-chloropropane	1,2,4-Trichlorobenzene
Hexachlorobutadiene	Naphthalene
1,2,3-Trichlorobenzene	

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Instrumentation and Methods

- GERSTEL MPS Prepstation, one rail configured for headspace analysis, the second rail for liquid addition
- Agilent 5973 or 5975 inert GC-MS system
- GERSTEL Maestro software
- Agilent ChemStation
- Anatune 240 position tray
- Anatune CoolR^{plus}

Sample Preparation

If manual internal standard and surrogate solution addition is to be performed, anhydrous sodium sulphate must be weighed into the required number of vials before adding the sample, adding the internal standard and surrogate solution and capping the vial.

If the MPS Prepstation is to add internal standard and surrogate solution, anhydrous sodium sulphate must be weighed into the required number of vials before adding the sample and capping the vial.

Results

Two calibration curves were prepared; one manually and the MPS Prepstation prepared the other. 160 additional samples were manually spiked with 100µg/L of the VOC standards listed above. The MPS Prepstation was used to add internal standard and surrogate solutions to these samples in a "just-in-time" manner.

The MCERTS criteria for precision and accuracy were used as a guide for the quality of the results. These criteria state that the %RSD of the surrogate and analyte 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, surrogates and analytes were spiked at 100µg/L, so a concentration between 70 and 130µg/L meets the regulatory criteria.

Table 1 shows the correlation coefficients obtained for each analytes' calibration curve, the mean concentration, standard deviation and relative standard deviation for each analyte using both standard curves as detailed above.

240 additional blank samples were prepared. To these vials, the MPS Prepstation added internal standard and surrogate solutions. The mean abundance and %RSD figures for each internal standard from the entire batch of 240 samples are listed below:

Internal Standard	Mean Abundance	% RSD
Pentafluorobenzene	28614331.37	9.91
Difluorobenzene	36178592.78	10.61
Chlorobenzene-d5	15734441.63	10.25
1,4-Dichlorobenzene-d4	18727709.07	9.83

The mean concentration, %RSD and bias figures for each surrohate from the entire batch of 240 samples spiked at 100µg/L are listed below:

Surrogate Analytes	Mean Calculated Concentration (µg/L)	% RSD	Bias (%)
1,2-Dichloroethane-d6	101.78	1.62	+1.78
Toluene-d8	99.53	1.40	-0.47
4-Bromofluorobenzene	101.06	1.43	+1.06

Figures 1, 2 and 3 show the calculated concentrations of each of the three surrogate analytes that had been added to 240 headspace vials in a "just-in-time" fashion prior to their analysis by the GERSTEL MPS Prepstation at a concentration of 100µg/L.

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Standard curve constructed manually							Standard curve constructed entirely by the MPS Prepstation						
Internal Standards	**r^2**	**Acceptable regulatory range**	**Mean concentration (n=160)**	**SD**	**% RSD**	**Bias (%)**	**Internal Standards**	**r^2**	**Acceptable regulatory range**	**Mean concentration (n=160)**	**SD**	**% RSD**	**Bias (%)**
Pentafluorobenzene	N/A	N/A	690638.97	45779.47	6.63	N/A	Pentafluorobenzene	N/A	N/A	690638.73	45779.63	6.63	N/A
Difluorobenzene	N/A	N/A	1089287.14	72696.26	6.67	N/A	Difluorobenzene	N/A	N/A	1089288.09	72696.22	6.67	N/A
Chlorobenzene-d5	N/A	N/A	462925.03	31711.90	6.85	N/A	Chlorobenzene-d5	N/A	N/A	462925.03	31711.90	6.85	N/A
1,4-Dichlorobenzene-d4	N/A	N/A	500771.92	32584.90	6.51	N/A	1,4-Dichlorobenzene-d4	N/A	N/A	500771.92	32584.90	6.51	N/A
Surrogates							**Surrogates**						
1,2-Dichloroethane-d6	N/A	70 – 130	97.41	1.92	1.97	-2.59	1,2-Dichloroethane-d6	N/A	70 – 130	99.25	1.95	1.97	-0.75
Toluene-d8	N/A	70 – 130	100.50	0.96	0.96	0.50	Toluene-d8	N/A	70 – 130	100.21	0.96	0.96	0.21
4-Bromofluorobenzene	N/A	70 – 130	98.59	1.47	1.50	-1.41	4-Bromofluorobenzene	N/A	70 – 130	100.42	1.50	1.50	0.42
Analytes							**Analytes**						
Chloroethane	1.000	70 – 130	90.14	3.88	4.31	-9.86	Chloroethane	1.000	70 – 130	95.78	4.13	4.31	-4.22
Bromomethane	1.000	70 – 130	80.09	5.20	6.49	-19.91	Bromomethane	1.000	70 – 130	85.79	5.62	6.55	-14.21
Trichlorofluoromethane	1.000	70 – 130	90.44	3.91	4.33	-9.56	Trichlorofluoromethane	1.000	70 – 130	95.82	4.16	4.34	-4.18
1,1-Dichloroethene	1.000	70 – 130	92.28	3.81	4.13	-7.72	1,1-Dichloroethene	1.000	70 – 130	98.70	4.06	4.12	-1.30
trans-1,2-Dichloroethene	1.000	70 – 130	93.20	4.20	4.50	-6.80	trans-1,2-Dichloroethene	1.000	70 – 130	99.72	4.49	4.50	-0.28
1,1-Dichloroethane	1.000	70 – 130	96.09	3.80	3.96	-3.91	1,1-Dichloroethane	1.000	70 – 130	103.32	4.11	3.98	3.32
cis-1,2-Dichloroethene	1.000	70 – 130	95.14	4.10	4.31	-4.86	cis-1,2-Dichloroethene	1.000	70 – 130	101.05	4.37	4.32	1.05
Chloroform	1.000	70 – 130	95.68	3.98	4.16	-4.32	Chloroform	1.000	70 – 130	102.63	4.30	4.19	2.63
Bromochloromethane	1.000	70 – 130	97.72	4.29	4.39	-2.28	Bromochloromethane	1.000	70 – 130	104.21	4.59	4.40	4.21
1,1,1-Trichloroethane	1.000	70 – 130	95.29	4.03	4.23	-4.71	1,1,1-Trichloroethane	1.000	70 – 130	100.78	4.25	4.22	0.78
1,1-Dichloropropene	0.999	70 – 130	94.18	4.10	4.35	-5.82	1,1-Dichloropropene	1.000	70 – 130	99.96	4.36	4.36	-0.04
1,2-Dichloroethane	0.999	70 – 130	95.35	4.04	4.23	-4.65	1,2-Dichloroethane	1.000	70 – 130	103.00	4.39	4.26	3.00
Benzene	1.000	70 – 130	94.92	3.87	4.08	-5.08	Benzene	1.000	70 – 130	100.77	4.10	4.07	0.77
1,2-Dichloropropane	0.999	70 – 130	96.57	4.03	4.17	-3.43	1,2-Dichloropropane	1.000	70 – 130	104.14	4.35	4.17	4.14
Trichloroethene	0.998	70 – 130	97.17	4.31	4.44	-2.83	Trichloroethene	1.000	70 – 130	103.24	4.60	4.46	3.24
Bromodichloromethane	1.000	70 – 130	95.33	4.05	4.25	-4.67	Bromodichloromethane	1.000	70 – 130	101.64	4.32	4.25	1.64
Dibromomethane	0.999	70 – 130	96.39	4.27	4.43	-3.61	Dibromomethane	1.000	70 – 130	104.77	4.65	4.44	4.77
cis-1,3-Dichloropropene	0.999	70 – 130	74.78	9.79	13.09	-25.22	cis-1,3-Dichloropropene	0.999	70 – 130	80.32	10.56	13.15	-19.68
Toluene	0.999	70 – 130	91.36	4.13	4.52	-8.64	Toluene	1.000	70 – 130	99.86	4.46	4.46	-0.14
1,1,2-Trichloroethane	1.000	70 – 130	96.54	4.20	4.35	-3.46	1,1,2-Trichloroethane	1.000	70 – 130	104.80	4.56	4.35	4.80
Carbon tetrachloride	1.000	70 – 130	94.93	4.28	4.51	-5.07	Carbon tetrachloride	1.000	70 – 130	99.60	4.46	4.48	-0.40
1,3-Dichloropropane	1.000	70 – 130	97.51	4.47	4.59	-2.49	1,3-Dichloropropane	1.000	70 – 130	103.06	4.71	4.57	3.06
Tetrachloroethene	1.000	70 – 130	93.46	5.17	5.53	-6.54	Tetrachloroethene	1.000	70 – 130	98.11	5.42	5.52	-1.89
Dibromochloromethane	1.000	70 – 130	97.49	4.51	4.63	-2.51	Dibromochloromethane	1.000	70 – 130	103.13	4.77	4.62	3.13
1,2-Dibromomethane	1.000	70 – 130	97.44	4.48	4.60	-2.56	1,2-Dibromomethane	1.000	70 – 130	101.05	4.61	4.57	1.05
Chlorobenzene	1.000	70 – 130	94.84	4.84	5.10	-5.16	Chlorobenzene	0.999	70 – 130	99.37	5.04	5.07	-0.63

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Standard curve constructed manually							Standard curve constructed entirely by the MPS Prepstation						
Analytes	**r^2**	**Acceptable regulatory range**	**Mean concentration (n=160)**	**SD**	**% RSD**	**Bias (%)**	**Analytes**	**r^2**	**Acceptable regulatory range**	**Mean concentration (n=160)**	**SD**	**% RSD**	**Bias (%)**
1,1,1,2-Tetrachloroethane	1.000	70 – 130	96.05	4.47	4.65	-3.95	1,1,1,2-Tetrachloroethane	0.999	70 – 130	101.62	4.70	4.63	1.62
Ethyl benzene	1.000	70 – 130	92.39	4.66	5.05	-7.61	Ethyl benzene	0.999	70 – 130	97.54	4.89	5.01	-2.46
m,p-Xylene	0.999	70 – 130	92.07	4.96	5.39	-7.93	m,p-Xylene	0.999	70 – 130	96.73	5.19	5.36	-3.27
o-Xylene	1.000	70 – 130	93.62	4.61	4.92	-6.38	o-Xylene	0.999	70 – 130	98.19	4.83	4.92	-1.81
Styrene	0.999	70 – 130	90.26	5.25	5.82	-9.74	Styrene	0.999	70 – 130	95.39	5.52	5.78	-4.61
Bromoform	1.000	70 – 130	96.97	4.44	4.58	-3.03	Bromoform	1.000	70 – 130	102.89	4.70	4.57	2.89
Isopropylbenzene	1.000	70 – 130	93.34	4.55	4.88	-6.66	Isopropylbenzene	0.999	70 – 130	98.56	4.79	4.86	-1.44
1,1,2,2-Tetrachloroethane	1.000	70 – 130	92.36	5.24	5.68	-7.64	1,1,2,2-Tetrachloroethane	1.000	70 – 130	99.00	5.62	5.68	-1.00
1,2,3-Trichloropropane	1.000	70 – 130	94.90	4.45	4.69	-5.10	1,2,3-Trichloropropane	1.000	70 – 130	101.74	4.80	4.72	1.74
n-Propylbenzene	1.000	70 – 130	91.35	5.31	5.82	-8.65	n-Propylbenzene	0.999	70 – 130	95.55	5.52	5.78	-4.45
Bromobenzene	1.000	70 – 130	92.41	5.05	5.47	-7.59	Bromobenzene	0.999	70 – 130	97.11	5.26	5.42	-2.89
2-Chlorotoluene	1.000	70 – 130	91.75	5.20	5.66	-8.25	2-Chlorotoluene	1.000	70 – 130	98.46	5.57	5.66	-1.54
1,3,5-Trimethylbenzene	1.000	70 – 130	89.94	5.23	5.82	-10.06	1,3,5-Trimethylbenzene	0.999	70 – 130	95.19	5.51	5.78	-4.81
4-Chlorotoluene	1.000	70 – 130	89.38	6.39	7.15	-10.62	4-Chlorotoluene	1.000	70 – 130	94.66	6.76	7.14	-5.34
tert-Butylbenzene	1.000	70 – 130	95.25	4.47	4.69	-4.75	tert-Butylbenzene	0.999	70 – 130	100.58	4.68	4.66	0.58
1,2,4-Trimethylbenzene	0.999	70 – 130	87.50	5.87	6.70	-12.50	1,2,4-Trimethylbenzene	0.999	70 – 130	93.54	6.23	6.66	-6.46
sec-Butylbenzene	0.999	70 – 130	91.57	4.39	4.79	-8.43	sec-Butylbenzene	1.000	70 – 130	96.89	4.65	4.80	-3.11
p-Isopropyltoluene	0.999	70 – 130	87.59	4.97	5.67	-12.41	p-Isopropyltoluene	0.999	70 – 130	92.79	5.26	5.67	-7.21
1,3-Dichlorobenzene	1.000	70 – 130	86.22	6.87	7.97	-13.78	1,3-Dichlorobenzene	0.999	70 – 130	90.70	7.19	7.93	-9.30
1,4-Dichlorobenzene	0.999	70 – 130	87.03	7.34	8.43	-12.97	1,4-Dichlorobenzene	1.000	70 – 130	91.79	7.83	8.53	-8.21
n-Butylbenzene	0.999	70 – 130	85.00	5.51	6.48	-15.00	n-Butylbenzene	1.000	70 – 130	89.95	5.85	6.51	-10.05
1,2-Dichlorobenzene	1.000	70 – 130	89.61	5.71	6.37	-10.39	1,2-Dichlorobenzene	1.000	70 – 130	94.95	6.05	6.37	-5.05
1,2-Dibromo-3-chlorpropane	0.999	70 – 130	97.14	4.45	4.58	-2.86	1,2-Dibromo-3-chlorpropane	0.999	70 – 130	103.38	4.74	4.59	3.38
1,2,4-Trichlorobenzene	1.000	70 – 130	78.70	10.32	13.12	-21.30	1,2,4-Trichlorobenzene	0.999	70 – 130	83.27	10.88	13.07	-16.73
Hexachlorobutadiene	1.000	70 – 130	79.99	8.27	10.33	-20.01	Hexachlorobutadiene	0.998	70 – 130	87.46	9.12	10.43	-12.54
Naphthalene	1.000	70 – 130	87.08	6.56	7.54	-12.92	Naphthalene	0.999	70 – 130	93.57	7.07	7.55	-6.43
1,2,3-Trichlorobenzene	1.000	70 – 130	81.83	8.85	10.82	-18.17	1,2,3-Trichlorobenzene	0.999	70 – 130	88.62	9.59	10.82	-11.38

Table 1 shows comparative data between a manually constructed calibration curve and a calibration curve constructed entirely by the MPS Prepstation prior to spiking the internal standards and surrogates and their headspace analysis in a "just-in-time" manner.

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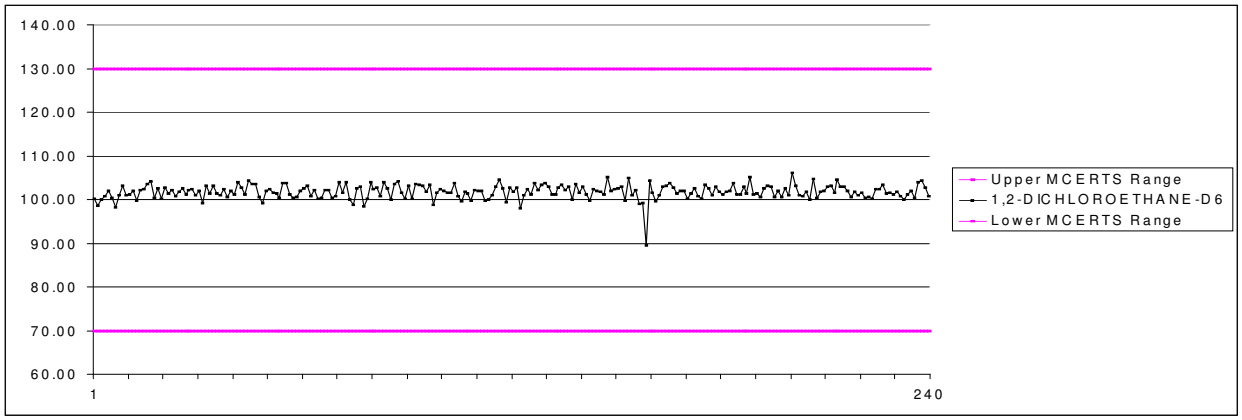

Figure 1

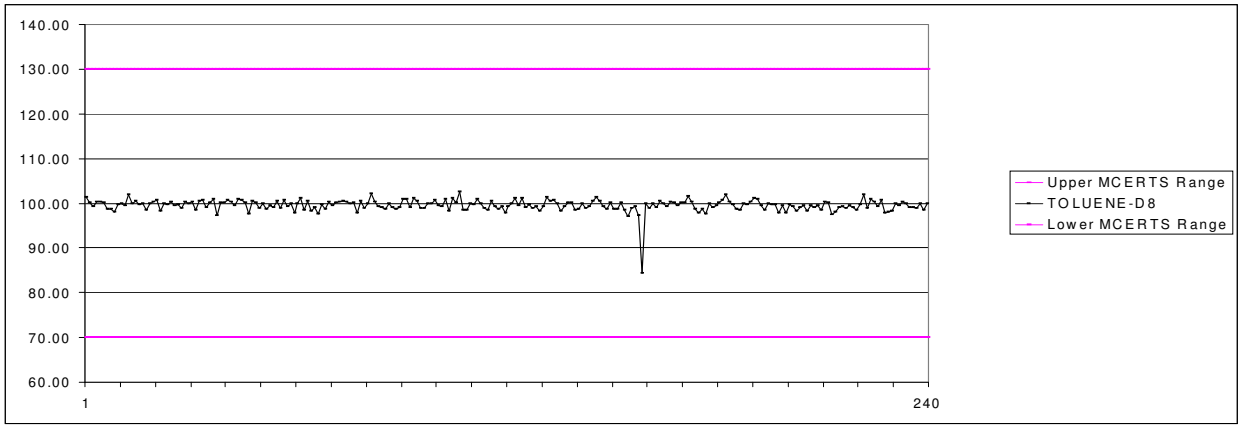

Figure 2

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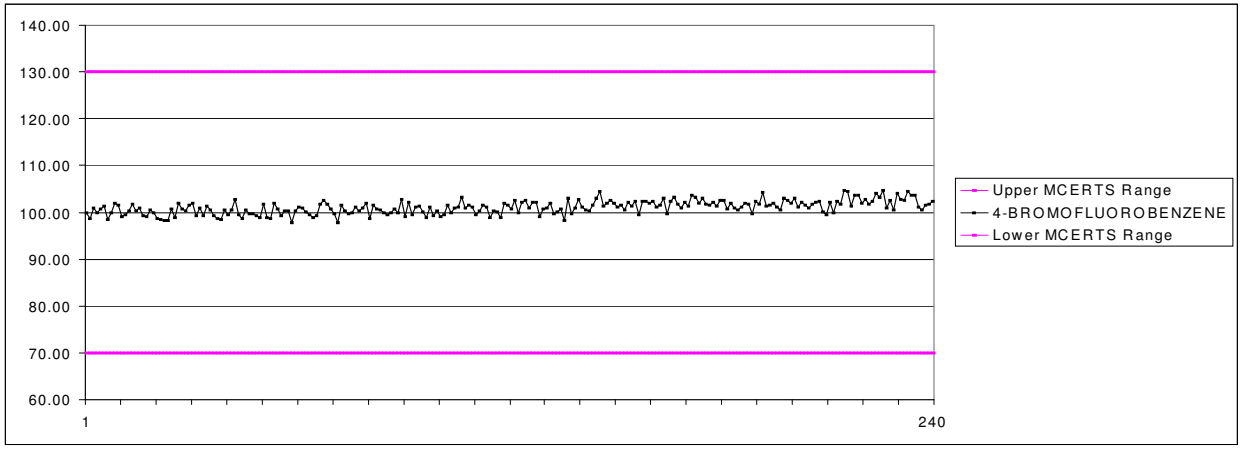

Figure 3

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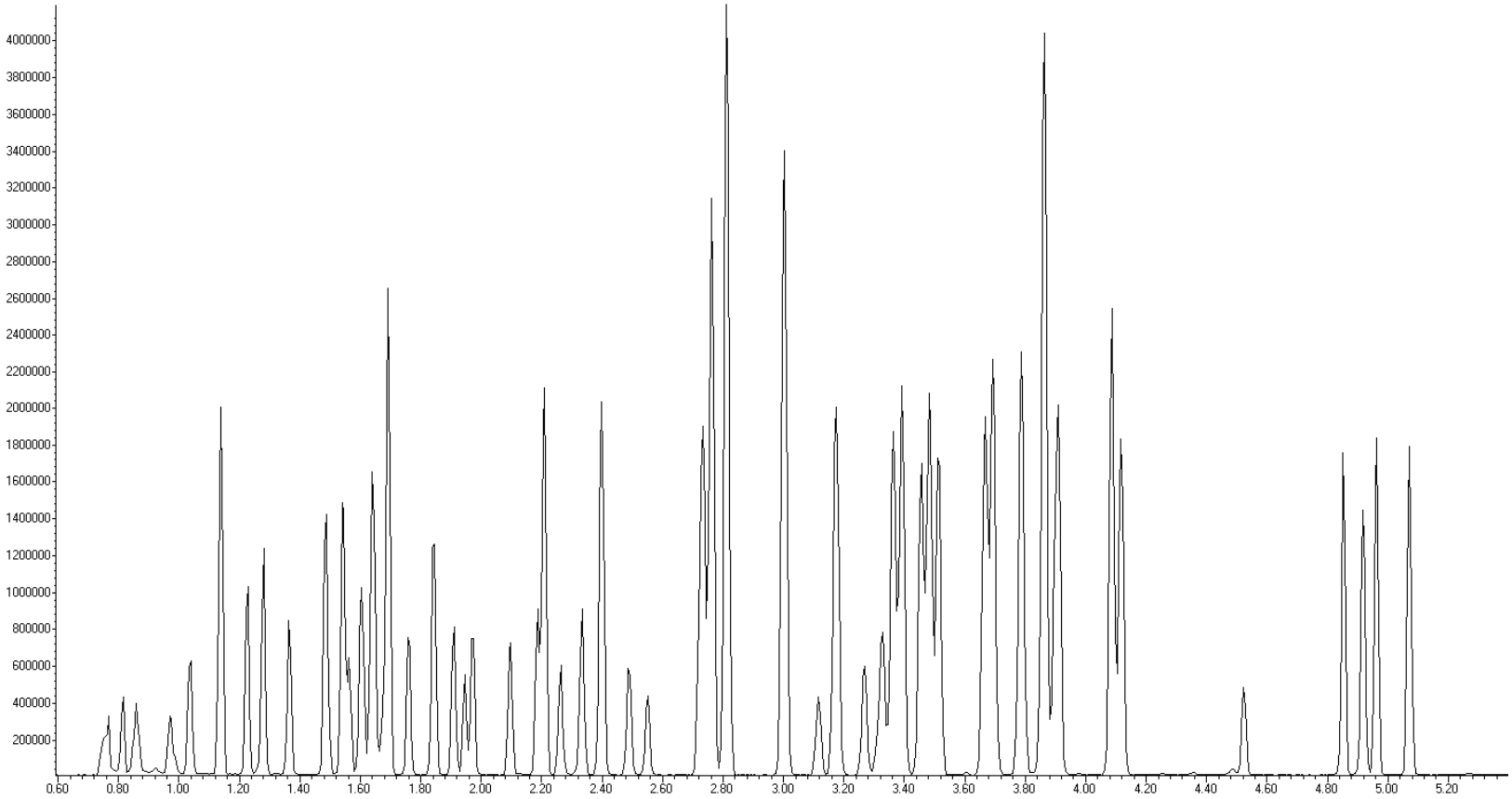

Figure 4 shows a chromatogram of a 200µg/L standard

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Conclusions

The spiking of volatile standards, 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 the addition of standards, internal standards and surrogates into both calibration and analytical samples is a practical proposition. This can be used to save both skilled analyst's valuable time and further reduce the opportunity for human error in the analytical process.

This work demonstrates that the automated addition of standards by the MPS Prepstation and Maestro software enables the construction of calibration curves that have correlation coefficients for individual analytes that are at least as good as those obtained from standards that have been prepared manually.

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