Automated Dilutions Using the Centurion Autosampler

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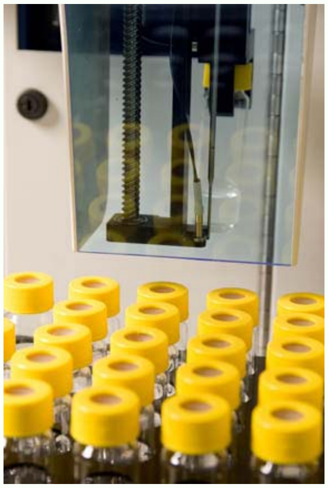
Introduction

Analysis of field samples in environmental laboratories can sometimes be complicated by how contaminated or “hot” the sample is. Many times “hot” samples have to be diluted in order to verify the level of contamination in the sample. The process of diluting samples is a time consuming process that can sometimes lead to human error when calculations are incorrect. A further problem is the loss of volatile organic compounds as the sample vial needs to be opened in order to perform the dilution.

This poster will examine the benefits of automated dilutions. Since the syringe option of this system has the unique ability to dilute samples from two times to 400 times the original concentration, this study will examine the precision and accuracy for an array of dilutions in this comprehensive range. The dilution data will be compared to a manually prepared 50ppb calibration standard in order to determine the accuracy of the results. The precision will be established by examining four sequential dilutions and the percent relative standard deviation of the compounds’ respective area counts. Furthermore, in order to demonstrate the linearity of the dilutions, a calibration curve will be presented using the automated dilution option to prepare 200ppb standards for a calibration range of 0.5ppb (400x) to 200ppb (1x).

Discussion

Environmental laboratories often have to dilute field samples due to the analytes of interest having concentrations over the highest calibration level of the curve. In order to dilute these samples, the vial has to be opened and a portion of the sample has to be diluted manually and re-analyzed. Opening the vial can compromise the integrity of the sample as volatiles are lost when the seal of the vial is broken.



EST Analytical has developed a syringe feature for the Centurion Autosampler that can dilute samples up to 400 times the original concentration. This feature is fully programmable and the sample vial does not have to be compromised in order to dilute the sample because the dilution process is automated. The sealed vial can be placed in the sample tray while the Centurion does all of the work.

Experimental

The Centurion WS autosampler was configured with an Encon Evolution concentrator. A Vocarb 3000 (K) trap was installed in the Evolution. Finally, the sampling system was connected to a GC/MS for sample analysis. The GC column employed for this study was an

Rxi-624Sil MS 30m x 0.25mm x 1.4µm. See Tables 1, 2 and 3 for Dilution Factor, Purge and Trap, and GC/MS parameters respectively.

Standard Concentration	Dilution Factors
100ppb	2x
250ppb	5x
500ppb	10x
2.5ppm	50x
5ppm	100x
10ppm	200x
20ppm	400x

Table 1: Dilution Factors

Purge and Trap Concentrator	EST Encon Evolution
Trap Type	Vocarb 3000
Valve Oven Temp.	150ºC
Transfer Line Temp.	150ºC
Trap Temp.	35ºC
Moisture Reduction Trap (MoRT) Temp.	39ºC
Purge Time	11 min.
Purge Flow	40mL/min
Dry Purge Temp.	ambient
Dry Purge Flow	40mL/min
Dry Purge Time	1.0 min.
Desorb Pressure Control	On
Desorb Pressure	5psi
Desorb Time	0.5 min.
Desorb Preheat Delay	5 sec.
Desorb Temp.	260ºC
Moisture Reduction Trap (MoRT) Bake Temp.	230ºC
Bake Temp	265ºC
Sparge Vessel Bake Temp.	120ºC
Bake Time	8
Bake Flow	40mL/min
Purge and Trap Auto-Sampler	**EST Centurion WS**
Sample Size	5mL
Internal Standard Volume	5µL

Table 2: Purge and Trap Parameters

GC/MS	Agilent 7890A/5975C inert XL
Inlet	Split/Splitless
Inlet Temp.	200ºC
Inlet Head Pressure	12.153 psi
Mode	Split
Split Ratio	40:1
Column	Rxi-624Sil MS 30m x 0.25mm I.D. 1.4µm film thickness
Oven Temp. Program	45ºC hold for 1 min., ramp 18ºC/min to 220ºC, hold for 0.3 min.
Column Flow Rate	1.0mL/min
Gas	Helium
Total Flow	44mL/min
Source Temp.	230ºC
Quad Temp.	150ºC
MS Transfer Line Temp.	180ºC
Scan Range	m/z 35-265
Scans	3.12 scans/sec
Solvent Delay	0.7 min.

Table 3: GC/MS Parameters

A 9 point calibration curve was manually prepared and run from 0.5 to 200ppb with standards ordered from Restek. After a linear calibration curve was established, a 50ppb calibration standard was run to establish instrument response for the compounds being analyzed. Next, a series of dilutions were run and compared with the initial 50ppb calibration standard. Each dilution factor was run four times with blanks in between. The final concentration of each dilution was 50ppb. The precision and accuracy of the dilutions are listed in Tables 4 and 5 and Figures 1 and 2 display the chromatograms of two of the dilutions.

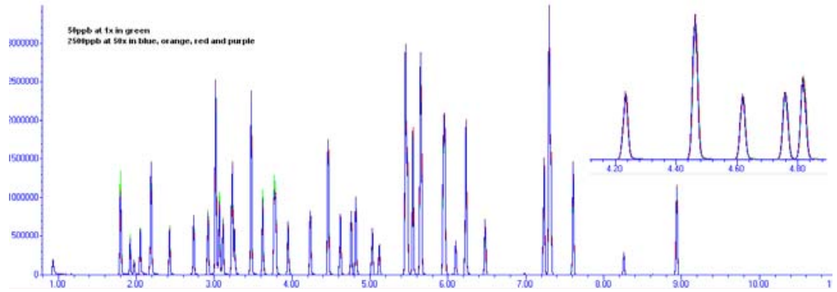


Figure 1: Overlay of 50ppb (1X) and 2500ppb (50x) Standards

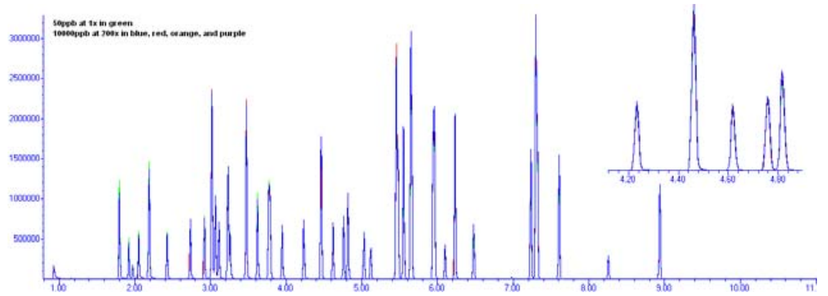


Figure 2: Overlay of 50ppb (1X) and 10000ppb (200x) Standards

Compound	Dilution							
	2x		5x		10x		50x	
	Precision (%RSD) 50ppb	Accuracy 50ppb	Precision (%RSD) 50ppb	Accuracy 50ppb	Precision (%RSD) 50ppb	Accuracy 50ppb	Precision (%RSD) 50ppb	Accuracy 50ppb
1,1-Dichloroethene	2.58	109.27	3.21	111.48	4.69	100.42	4.50	86.27
Methylene Chloride	0.63	106.49	1.35	111.23	4.74	99.01	2.63	92.39
MTBE	0.86	100.60	0.41	108.40	5.31	96.09	2.52	93.49
trans-1,2-Dichloroethene	1.24	109.61	1.72	113.24	5.05	100.87	2.99	95.78
1,1-Dichloroethane	1.74	108.42	2.20	112.17	4.75	100.16	3.46	95.16
cis-1,2-Dichloroethene	1.86	109.70	2.43	112.18	4.51	100.88	4.10	93.08
Chloroform	0.87	105.85	1.19	110.99	5.15	98.98	2.81	99.89
1,1,1-Trichloroethane	0.98	102.57	1.10	109.51	4.78	96.65	2.23	100.07
Carbon Tetrachloride	2.76	106.89	2.64	110.52	4.73	100.55	4.41	96.61
Benzene	1.46	108.76	1.75	112.33	4.82	100.57	3.57	97.23
1,2-Dichloroethane	0.58	102.87	0.97	109.51	4.88	97.80	1.89	97.63
Trichloroethene	2.08	109.29	2.11	111.18	4.68	100.44	3.31	85.67
1,2-Dichloropropane	0.86	106.19	1.50	111.49	4.70	99.59	2.94	99.70
Bromodichloromethane	0.87	105.85	1.19	110.99	5.15	98.98	2.81	99.89
cis-1,3-Dichloropropene	1.34	108.49	1.09	108.60	5.92	93.91	4.59	101.04
Toluene	1.46	109.41	2.07	112.38	4.69	100.80	3.85	100.39
trans-1,3-Dichloropropene	0.73	106.00	1.21	108.01	6.05	93.40	4.05	101.50
1,1,2-Trichloroethane	0.98	102.57	1.10	109.51	4.78	96.65	2.23	100.07
Tetrachloroethene	1.87	108.55	2.52	110.40	4.46	99.16	3.77	98.01
Dibromochloromethane	0.83	103.11	0.80	109.10	5.49	96.92	2.38	101.53
1,2-Dibromoethane	0.83	101.20	0.92	109.08	5.33	97.60	2.25	100.49
Chlorobenzene	1.10	108.59	1.76	112.22	4.92	100.56	3.13	102.72
Ethylbenzene	1.38	109.37	1.95	112.21	4.92	100.98	3.53	102.44
Xylene (m+p)	1.28	109.20	1.76	112.19	4.95	100.67	3.71	102.84
Styrene	1.06	107.04	1.24	111.76	4.86	99.22	3.05	103.09
Xylene (o)	1.02	108.24	1.56	111.50	4.97	100.22	3.33	103.22
Bromoform	0.81	100.70	0.81	109.03	4.92	96.14	2.51	102.13
Isopropylbenzene	1.37	108.59	2.36	111.83	4.59	100.43	3.61	102.90
1,1,2,2-Tetrachloroethane	2.04	100.66	0.59	110.64	5.69	97.80	1.89	124.16
1,3-Dichlorobenzene	0.34	105.88	1.36	109.00	4.76	97.60	2.65	103.71
1,4-Dichlorobenzene	0.80	104.81	1.19	108.35	4.93	97.07	2.83	104.11
1,2,-Dichlorobenzene	0.80	103.86	0.59	107.90	4.80	96.78	2.68	104.41
1,2-Dibromo-3-chloropropane	1.56	96.58	1.15	106.59	5.39	93.78	2.41	102.04
1,2,4-Trichlorobenzene	0.42	100.14	1.34	104.64	5.34	93.01	2.37	99.45
Average	1.22	105.75	1.50	110.30	4.99	98.34	3.09	99.80

Table 4: Experimental Results (2x, 5x, 10x, and 50x dilutions)

Compound	Dilution					
	100x		200x		400x	
	Precision (%RSD) 50ppb	Accuracy 50ppb	Precision (%RSD) 50ppb	Accuracy 50ppb	Precision (%RSD) 50ppb	Accuracy 50ppb
1,1-Dichloroethene	3.18	87.82	2.75	82.78	5.09	88.21
Methylene Chloride	2.26	91.75	2.92	86.64	5.04	84.31
MTBE	2.33	91.48	3.06	85.75	2.75	83.69
trans-1,2-Dichloroethene	2.18	95.77	3.26	92.24	4.88	88.26
1,1-Dichloroethane	2.31	93.92	3.12	89.22	8.35	81.80
cis-1,2-Dichloroethene	2.30	93.70	3.46	91.35	5.17	92.71
Chloroform	2.04	99.86	3.04	96.84	4.38	91.84
1,1,1-Trichloroethane	2.24	99.21	2.79	96.72	2.29	90.43
Carbon Tetrachloride	2.78	101.17	3.34	98.32	4.98	93.64
Benzene	2.50	97.68	3.16	95.01	4.67	91.37
1,2-Dichloroethane	2.28	96.39	3.01	92.23	3.23	87.23
Trichloroethene	2.09	88.53	2.86	86.83	4.39	95.26
1,2-Dichloropropane	2.27	99.18	3.15	96.20	4.66	90.98
Bromodichloromethane	2.04	99.86	3.04	96.84	4.38	91.84
cis-1,3-Dichloropropene	2.53	97.94	4.26	91.38	4.43	89.87
Toluene	2.09	102.22	3.18	101.10	4.78	93.95
trans-1,3-Dichloropropene	2.11	98.61	4.47	91.20	4.07	94.04
1,1,2-Trichloroethane	2.24	99.21	2.79	96.72	2.29	90.43
Tetrachloroethene	2.60	104.72	2.88	104.59	5.17	94.60
Dibromochloromethane	2.28	101.62	2.74	98.28	2.86	93.32
1,2-Dibromoethane	2.55	100.61	2.87	97.26	2.62	91.40
Chlorobenzene	2.16	105.17	2.65	104.57	4.08	94.96
Ethylbenzene	2.74	106.99	3.16	105.77	5.13	92.60
Xylene (m+p)	2.68	107.15	3.15	105.95	5.11	92.77
Styrene	2.79	106.74	2.97	105.63	4.23	92.43
Xylene (o)	2.48	107.41	3.25	105.87	5.00	92.36
Bromoform	1.84	102.45	2.41	99.31	2.08	91.81
Isopropylbenzene	3.05	112.13	2.99	108.29	5.41	100.83
1,1,2,2-Tetrachloroethane	2.91	123.63	3.06	121.80	2.10	94.43
1,3-Dichlorobenzene	2.66	111.57	2.97	110.16	4.72	92.72
1,4-Dichlorobenzene	2.43	111.47	2.98	111.15	4.11	92.27
1,2,-Dichlorobenzene	2.16	111.49	2.78	109.90	3.76	91.83
1,2-Dibromo-3-chloropropane	2.52	101.98	3.93	99.83	4.17	94.78
1,2,4-Trichlorobenzene	1.98	113.98	2.64	105.95	3.92	90.51
Average	2.40	101.86	3.09	98.87	4.24	91.57

Table 5: Experimental Results (100x, 200x and 400x dilutions)

Finally, a nine point calibration curve was run by setting up the system to do the dilutions. The curve was run using nine 40ml vials filled to volume with a 200ppb calibration standard and doing serial dilutions on the standards. For example, the 200ppb was diluted 400x for the 0.5ppb standard, 200x for the 1.0ppb standard, etc. See Table 6 for the curve dilutions and Table 7 for the curve linearity and compound responses.

Standard Concentration	Dilution Factors	Final Concentration
200ppb	400x	0.5ppb
200ppb	200x	1ppb
200ppb	100x	2ppb
200ppb	50x	4ppb
200ppb	20x	10ppb
200ppb	10x	20ppb
200ppb	4x	50ppb
200ppb	2x	100ppb
200ppb	1x	200ppb

Table 6: Syringe Curve Dilutions

Compound	Ave RF	Curve %RSD	Compound	Ave RF	Curve %RSD
Dichlorofluoromethane	0.526	8.28	1,3-Dichloropropane	0.789	5.70
Chloromethane	0.706	3.61	Dibromochloromethane	0.345	13.51
Vinyl Chloride	0.654	8.56	2-Hexanone	0.447	10.44
Bromomethane	0.322	12.86	1,2-Dibromoethane	0.383	7.60
Chloroethane	0.381	4.72	Chlorobenzene	1.373	3.86
Trichlorofluoroethane	0.698	12.45	1,1,1,2-Tetrachloroethane	0.410	9.83
1,1-Dichloroethene	0.420	6.29	Ethylbenzene	2.670	4.83
Acetone	0.185	9.98	Xylene (p&m)	2.058	4.72
Iodomethane	0.300	*0.999	Styrene	1.521	5.68
Carbon Disulfide	1.410	11.20	Xylene (o)	2.082	3.81
Methylene Chloride	0.486	6.16	Bromoform	0.235	*0.997
MTBE	1.380	11.16	Isopropylbenzene	2.417	5.54
trans-1,2-dichoroethene	0.461	5.09	Bromobenzene	2.911	4.86
1,1-Dichloroethane	0.953	6.15	1,2,3-Trichloropropane	1.236	9.20
cis-1,2-dichloroethene	0.492	4.68	1,1,2,2-Tetrachloroethane	1.428	7.26
2-Butanone	0.954	8.87	n-Propylbenzene	6.676	6.30
2,2-Dichloropropane	0.641	5.11	2-Chlorotoluene	1.091	3.86
Bromochloromethane	0.250	4.14	4-Chlorotoluene	1.126	4.25
Chloroform	0.830	3.41	1,3,5-Trimethylbenzene	5.295	6.02
1,1,1-Trichloroethane	0.643	6.90	tert-Butylbenzene	3.657	7.89
2-Chloroethylvinylether	0.373	10.62	sec-Butylbenzene	0.992	7.35
Carbon Tetrachloride	0.497	5.07	1,2,4-Trimethylbenzene	4.320	6.17
1,1-Dichloropropene	0.757	8.10	1,3-Dichlorobenzene	2.057	7.58
Benzene	2.047	3.66	1,4-Dichlorobenzene	2.094	7.89
1,2-Dichloroethane	0.675	6.21	Isopropyltoluene	4.301	6.43
Trichloroethene	0.444	5.04	1,2-Dichlorobenzene	1.197	5.32
1,2-Dichloropropane	0.556	6.25	n-Butylbenzene	4.377	8.85
Dibromomethane	0.234	10.94	1,2-Dibromo-3-chloropropane	0.249	13.10
Bromodichloromethane	0.575	12.61	1,2,4-Trichlorobenzene	1.230	12.15
cis-1,3-Dichloropropene	0.765	9.69	Naphthalene	3.667	8.30
Toluene	1.197	3.83	Hexachlorobutadiene	0.514	13.76
trans-1,3-Dichloropropene	0.692	10.44	1,2,3-Trichlorobenzene	1.113	12.28
1,1,2-Trichloroethane	0.386	8.07	Average	1.113	7.51
Tetrachloroethane	0.383	6.20	*Curve Results were linear regressed.		

Table 7: Automated Dilution Curve Results

Conclusions

The Centurion WS with the syringe option displayed remarkable precision and accuracy from as low as the 2x dilution to as high as 400x dilution. On the whole, the average precision of the instrument was less than 5%RSD while the overall accuracy was 90% to 110%. The system also is capable of curve automation with the average %RSD of below 10% for a 9 point curve from 0.5ppb to 200ppb. The automated dilution feature of the Centurion WS with the syringe option would enable laboratories to run samples more efficiently and the since the samples would not need to be compromised in order to perform dilutions, the accuracy of the experimental results would improve.