Application Note

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ePrep Sample Preparation Workstation | Application Note 20194

Automated Standard Preparation for Purge & Trap USEPA Method 8260

ABSTRACT

The preparation of Volatile Organic Standards (VOCs) for the United States Environmental Protection Agency (USEPA) Method 8260D1 is a tedious prospect. Standards need to be prepared every day. Calibration and laboratory control standards are run every 12 hours and Matrix Spike/Matrix Spike duplicate samples are required for every 20 samples or each batch. Since the analytes in Method 8260D are volatile, standard preparation can be challenging. This application will demonstrate the capability to automate standard preparation for volatile organic standards.

Figure 1 ePrep Sample Preparation Workstation

INTRODUCTION

Standards for VOC labs need to be prepared every day. There are method requirements that need to be met in order to prove that the sampling and analysis systems are working properly. The preparation of these standards on top of the stock standards and calibration curves can have the propensity to be very time-consuming. Furthermore, the Human Error Probability (HEP) can be high. "Human error is inevitable in measuring an amount-of-substance concentration and testing chemical composition".[2] This can result in lost time, wasted labour, and delayed customer results and satisfaction.

Volatile standards can be tricky to prepare. Stock standards require multiple mixes in order to encompass the entire list of compounds, and calibration, CCV, and LCS water standards require full forty millilitre vials with no headspace. The **ePrep sample preparation workstation** (Figure 1) utilizes gas-tight syringes in order to accurately transfer volatile liquids. It also has software specially designed to customize workflows to laboratory requirements. For this application, the ePrep sample preparation workstation automated all of the sample preparation for USEPA Method 8260D. The **EST Analytical Evolution and Centurion Purge and Trap** (Figure 2) were employed for sample transfer and purge and trap sampling.

EXPERIMENTAL

Automated standard preparation was performed by the ePrep. USEPA Method 8260D standards were procured and transferred into 2mL vials. The two mL vials were then placed on the ePrep and using the ePrep software, stock standards were prepared. Table 1 outlines the stock standard formulation workflow. Once the stock standards were made, a calibration curve was created using the ePrep workflow summarized in Table 2. The calibration standards were used in order to define a nine point calibration curve with a range of 0.46 to 186µg/L.

Figure 2 EST Purge and Trap System

ePrep Workflow for Volatile Stock Standards				
Step	**Volume**	**Tool Wash Aspirate Flowrate**	**Input Group**	**Output Group**
Extra Tool Wash	600 µL	40 µL/sec	Syringe Wash	Waste
Add Diluent	200 µL	70 µL/sec	Standard Solvent	200 mg/L standard
Extra Tool Wash	30 µL	20 µL/sec	Syringe Wash	Waste
Add Diluent	40 µL	60 µL/sec	VOA Cal Mix 1	200 mg/L standard
Extra Tool Wash	30 µL	20 µL/sec	Syringe Wash	Waste
Add Diluent	80 µL	60 µL/sec	Surrogate Standard	200 mg/L standard
Extra Tool Wash	30 µL	20 µL/sec	Syringe Wash	Waste
Batch Many to Many	100 µL	60 µL/sec	VOA Cal Standards	200 mg/L standard
Extra Tool Wash - Post Task	30 µL	20 µL/sec	Syringe Wash	Waste
Make Up to Volume	1000 µL	70 µL/sec	Standard Solvent	200 mg/L standard
Shake (1500rpm for 30 seconds)				200 mg/L standard
Extra Tool Wash	250 µL	40 µL/sec	Syringe Wash	Waste
Add Diluent	500 µL	70 µL/sec	Standard Solvent	20 mg/L standard
Add Diluent	100 µL	60 µL/sec	200 ppm standard	20 mg/L standard
Extra Tool Wash	30 µL	20 µL/sec	Syringe Wash	Waste
Make Up to Volume	1000 µL	70 µL/sec	Standard Solvent	20 mg/L standard
Shake (1500rpm for 30 seconds)				20 mg/L standard
Add Diluent	500 µL	70 µL/sec	Standard Solvent	2 mg/L standard
Add Diluent	100 µL	60 µL/sec	20 ppm	2 mg/L standard
Extra Tool Wash	30 µL	20 µL/sec	Syringe Wash	Waste
Make Up To Volume	1000 µL	40 µL/sec	Standard Solvent	2 mg/L standard
Shake (1500rpm for 30 seconds)				2 mg/L standard

Table 1: ePrep Workflow for Stock Standards

ePrep Workflow for Volatile 9 Point Calibration Curve				
Step	**Volume**	**Tool Wash Aspirate Flowrate**	**Input Group**	**Output Group**
Extra Tool Wash	50 µL	20 µL/sec	Methanol Rinse	Waste
Add Internal Standard	10 µL	20 µL/sec	2 mg/L Standard	0.46 µg/L
Add Internal Standard	20 µL	20 µL/sec	2 mg/L Standard	0.93 µg/L
Add Internal Standard	40 µL	20 µL/sec	2 mg/L Standard	1.86 µg/L
Add Internal Standard	10 µL	20 µL/sec	20 mg/L Standard	4.65 µg/L
Add Internal Standard	20 µL	20 µL/sec	20 mg/L Standard	9.3 µg/L
Add Internal Standard	40 µL	20 µL/sec	20 mg/L Standard	18.6 µg/L
Add Internal Standard	10 µL	20 µL/sec	200 mg/L Standard	46.5 µg/L
Add Internal Standard	20 µL	20 µL/sec	200 mg/L Standard	93.0 µg/L
Add Internal Standard	40 µL	20 µL/sec	200 mg/L Standard	186.0µg/L

*Septum Free Pierce Mode

Table 2: ePrep Workflow for Calibration Standards

The EST Analytical Centurion WS Autosampler and Evolution purge and trap concentrator were interfaced to a Gas Chromatograph/Mass Spectrometer (GC/MS) and the optimal conditions required to achieve the desired chromatographic resolution and sensitivity over the entire compound list in compliance with all USEPA Method 8260D criteria1 were established. The Evolution was configured with a Vocarb 3000 trap and the Centurion was set to run water samples. A 30m x 0.25mm x 1.4µm Rxi 624 Sil MS column was installed in the GC while the MS was set to scan m/z 35 to 300. The calibration samples prepared by the ePrep were placed on the sample rack of the Centurion WS for sampling and analysis. The purge and trap and GC/MS conditions used to obtain the results are listed in Tables 3 and 4.

Purge and Trap Concentrator	EST Analytical Evolution
Trap Type	Vocarb 3000
Valve Oven Temp.	140°C
Transfer Line Temp.	140°C
Trap Temp.	35°C
Moisture Reduction Trap (MoRT) Temp.	39°C
Purge Time	11 min
Purge Flow	40mL/min
Dry Purge Temp.	Off
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	10 sec
Desorb Temp.	250°C
Moisture Reduction Trap (MoRT) Bake Temp.	210°C
Bake Temp	250°C
Sparge Vessel Bake Temp.	110°C
Bake Time	6 min
Bake Flow	85mL/min
Purge and Trap Auto-Sampler	**EST Analytical Centurion WS**
Sample Type	Water
Sample Fill Mode	Loop
Sample Volume	5mL
Loop Fill Time	20 sec
Loop Equilibration Time	5 sec
Sample Transfer Time	10 sec
Sample Loop Rinse	On/20 sec
Sample Loop Sweep Time	15 sec
Number of Sparge Rinses	2
Rinse Volume	5mL
IS volume	5µL

Table 3: Evolution and Centurion WS Experimental Parameters

GC/MS	Agilent 7890B/5977B inert Plus
Inlet	Split/Splitless
Inlet Temp.	220°C
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	45°C hold for 1 min, ramp 15°C/min to 220°C, hold for 1.33 min, 14 min run time
Column Flow Rate	1mL/min
Gas	Helium
Total Flow	44mL/min
Source Temp.	230°C
Quad Temp.	150°C
MS Transfer Line Temp.	180°C
Scan Range	m/z 35-300
Scans	5.2 scans/sec
Solvent Delay	0.7 min

Table 4: GC/MS Parameters

After the calibration curve was established, the ePrep was employed to create Method Detection Limit (MDL) and precision and accuracy standards. The ePrep workflow parameters are summarized in Table 5. The MDL study was performed over the course of three days while the 30 precision and accuracy standards were all made on one day and five standards a day were run over the course of a week in order to test the stability of the standards over time. The precision and accuracy standards were stored in the refrigerator and brought to room temperature before they were sampled. The results of the calibration curve and MDL experiments are outlined in Table 6 while the precision and accuracy study outcomes are listed in Table 7. Figure 3 is a display of the 46.5µg/L chromatogram.

ePrep Workflow for MDLs and Precision and Accuracy				
Step	**Volume**	**Tool Wash Aspirate Flowrate**	**Input Group**	**Output Group**
Extra Tool Wash	30 µL	20µl/sec	Methanol Rinse	Waste
Add Internal Standard	10 µL	20µl/sec	2 mg/L	0.46 µg/L
Add Internal Standard	10 µL	20µl/sec	20 mg/L	4.65 µg/L
Add Internal Standard	10 µL	20µl/sec	200 mg/L	46.5 µg/L

*Septum Free Pierce Mode

Table 5: ePrep Workflow for MDL and Precision and Accuracy Standards

Compound	Curve RF	Curve %RSD	MDL	Compound	Curve RF	Curve %RSD	MDL
Dichlorodifluoromethane	0.822	5.16	0.18	2-nitropropane	0.188	7.52	0.18
Chloromethane	0.803	11.42	0.14	2-chloroethylvinyl ether	0.310	5.49	0.15
Vinyl Chloride	0.884	6.33	0.17	cis-1,3-Dichloropropene	0.672	6.25	0.13
Bromomethane	0.601	14.21	0.15	4-methyl-2-pentanone	0.515	10.30	0.18
Chloroethane	0.558	12.63	0.24	Toluene-d8 SUR	1.514	5.24	0.15
Trichlorofluoromethane	1.410	7.37	0.13	Toluene	1.112	6.34	0.17
diethyl ether	0.502	5.50	0.18	ethyl methacrylate	0.649	6.24	0.15
1,1,2-trichlorofluoroethane	0.723	6.58	0.18	trans-1,3-Dichloropropene	0.661	7.99	0.14
1,1-Dichloroethene	0.639	7.08	0.14	1,1,2-Trichloroethane	0.368	6.18	0.17
Acetone	0.266	10.42	0.71	Tetrachloroethene	0.421	6.48	0.14
Iodomethane	0.518	*0.996	0.10	1,3-Dichloropropane	0.649	5.78	0.16
Carbon Disulfide	1.834	8.75	0.15	Dibromochloromethane	0.450	4.76	0.16
allyl chloride	0.769	9.96	0.17	2-Hexanone	0.369	8.97	0.27
Methylene Chloride	0.609	11.38	0.17	isopropyl acetate	0.035	7.70	0.71
TBA	0.105	7.22	0.23	butyl acetate	0.331	8.70	0.19
MTBE	1.895	6.10	0.19	1,2-Dibromoethane	0.401	5.36	0.18
cis-1,2-Dichloroethene	0.711	7.43	0.17	Chlorobenzene	1.221	5.90	0.16
acrylonitrile	0.308	9.29	0.24	1,1,1,2-Tetrachloroethane	0.452	5.71	0.19
vinyl acetate	2.073	7.72	0.15	Ethylbenzene	2.289	8.07	0.19
Isopropylether	1.881	5.89	0.17	Xylene (m+p)	1.749	9.16	0.20
1,1-Dichloroethane	1.140	5.66	0.15	Styrene	1.319	4.32	0.17
Ethyl Tert Butyl Ether	1.923	5.61	0.13	Xylene (o)	1.733	7.99	0.19
Ethyl Acetate	0.128	11.33	0.70	n-amyl acetate	0.855	6.71	0.15
trans-1,2-Dichloroethene	0.656	8.68	0.19	Bromoform	0.359	6.09	0.15
2-Butanone	1.152	7.16	0.15	Isopropylbenzene	2.174	4.51	0.18
2,2-Dichloropropane	1.156	9.80	0.14	cis-1,4-dichloro-2-butene	0.076	5.14	0.89
Bromochloromethane	0.312	10.39	0.20	BFB SUR	1.178	7.97	0.17
propionitrile	0.130	12.32	1.07	Bromobenzene	2.054	6.95	0.18
methacrylonitrile	0.467	7.52	0.16	1,2,3-Trichloropropane	0.961	8.56	0.20
THF	0.246	8.98	0.84	1,1,2,2-Tetrachloroethane	1.178	7.34	0.16
Chloroform	1.196	7.23	0.13	n-Propylbenzene	4.976	6.05	0.19
methyl acrylate	0.723	5.80	0.17	trans-1,4-dichloro-2-butene	0.107	11.06	0.76
Dibromofluoromethane	0.650	11.58	0.14	2-Chlorotoluene	0.927	4.79	0.18
1,1,1-Trichloroethane	1.199	5.31	0.18	4-Chlorotoluene	0.955	6.54	0.22
Carbon Tetrachloride	1.091	4.80	0.15	1,3,5-Trimethylbenzene	3.284	4.31	0.18
1,1-Dichloropropene	1.035	5.83	0.15	tert-Butylbenzene	3.070	4.52	0.17

Methyl Acetate	0.645	4.86	0.25	sec-Butylbenzene	0.874	6.25	0.20
Isobutyl Alcohol	0.044	12.61	1.38	1,2,4-Trimethylbenzene	3.226	4.58	0.18
Tert Amyl Methyl Ether	1.843	5.69	0.13	1,3-Dichlorobenzene	1.712	5.61	0.19
Benzene	2.589	6.01	0.16	1,4-Dichlorobenzene	1.722	6.34	0.18
1,2-Dichloroethane	0.897	7.03	0.16	Isopropyltoluene	3.470	4.22	0.18
1,4-Dioxane	0.013	4.51	1.43	1,2,-Dichlorobenzene	1.599	5.23	0.14
Trichloroethene	0.489	4.81	0.16	n-Butylbenzene	3.017	5.02	0.17
1,2-Dichloropropane	0.401	4.55	0.17	1,2-Dibromo-3-chloroprop	0.263	7.06	0.20
methyl methacrylate	0.367	7.27	0.17	1,2,4-Trichlorobenzene	0.950	7.59	0.15
propyl acetate	0.711	6.09	0.17	Naphthalene	3.194	4.79	0.14
Dibromomethane	0.269	4.86	0.11	Hexachlorobutadiene	0.430	11.12	0.18
Bromodichloromethane	0.583	5.53	0.15	1,2,3-Trichlorobenzene	0.925	6.75	0.16

*weighted quadratic regression

Table 6: Calibration Curve and MDL Data Summary

Compound	%RSD Precision	%Rec'ry	Compound	%RSD Precision	%Rec'ry
Dichlorodifluoromethane	5.32	121.61	2-nitropropane	4.70	93.42
Chloromethane	4.27	100.55	2-chloroethylvinyl ether	4.26	95.21
Vinyl Chloride	5.10	105.53	cis-1,3-Dichloropropene	5.28	92.49
Bromomethane	4.06	97.77	4-methyl-2-pentanone	5.23	89.72
Chloroethane	5.08	97.85	Toluene-d8 SUR	4.67	94.82
Trichlorofluoromethane	6.10	103.43	Toluene	4.66	91.84
diethyl ether	4.43	98.82	ethyl methacrylate	3.90	92.80
1,1,2-trichlorofluoroethane	6.03	98.51	trans-1,3-Dichloropropene	5.48	91.55
1,1-Dichloroethene	5.37	98.19	1,1,2-Trichloroethane	4.06	95.23
Acetone	8.73	92.10	Tetrachloroethene	6.53	96.14
Iodomethane	4.93	113.74	1,3-Dichloropropane	4.05	94.95
Carbon Disulfide	4.96	100.08	Dibromochloromethane	4.12	98.78
allyl chloride	5.49	95.51	2-Hexanone	5.80	91.43
Methylene Chloride	4.42	94.15	isopropyl acetate	4.96	93.73
TBA	7.78	88.19	butyl acetate	4.44	88.64
MTBE	4.57	98.25	1,2-Dibromoethane	4.21	97.89
cis-1,2-Dichloroethene	4.49	97.46	Chlorobenzene	4.33	88.15
acrylonitrile	4.94	94.53	1,1,1,2-Tetrachloroethane	4.22	90.73
vinyl acetate	4.81	101.26	Ethylbenzene	5.21	85.15
Isopropylether	4.36	94.99	Xylene (m+p)	5.05	85.26
1,1-Dichloroethane	4.57	96.67	Styrene	4.36	90.19
Ethyl Tert Butyl Ether	4.54	96.83	Xylene (o)	4.72	85.90
Ethyl Acetate	5.11	89.06	n-amyl acetate	4.62	84.32
trans-1,2-Dichloroethene	4.82	96.53	Bromoform	3.99	94.04
2-Butanone	5.18	95.71	Isopropylbenzene	5.75	89.16
2,2-Dichloropropane	12.96	90.01	cis-1,4-dichloro-2-butene	4.62	91.82
Bromochloromethane	4.55	97.72	BFB SUR	4.06	80.68
propionitrile	5.64	95.83	Bromobenzene	4.05	81.06
methacrylonitrile	4.89	93.84	1,2,3-Trichloropropane	5.77	85.30
THF	6.01	96.47	1,1,2,2-Tetrachloroethane	4.06	83.25
Chloroform	4.41	96.75	n-Propylbenzene	5.74	82.48
methyl acrylate	4.86	98.49	trans-1,4-dichloro-2-butene	5.44	80.09
Dibromofluoromethane	4.32	97.20	2-Chlorotoluene	4.90	84.69
1,1,1-Trichloroethane	5.65	97.09	4-Chlorotoluene	4.54	83.68
Carbon Tetrachloride	6.01	99.64	1,3,5-Trimethylbenzene	5.09	84.41
1,1-Dichloropropene	5.61	96.97	tert-Butylbenzene	6.09	85.85
Methyl Acetate	3.95	97.21	sec-Butylbenzene	6.26	85.81
Isobutyl Alcohol	7.43	84.84	1,2,4-Trimethylbenzene	4.73	85.00
Tert Amyl Methyl Ether	4.52	97.97	1,3-Dichlorobenzene	4.25	86.57
Benzene	4.62	96.71	1,4-Dichlorobenzene	4.11	86.12
1,2-Dichloroethane	4.22	98.47	Isopropyltoluene	5.68	86.07
1,4-Dioxane	4.66	99.59	1,2,-Dichlorobenzene	3.94	87.23
Trichloroethene	5.05	95.54	n-Butylbenzene	5.97	85.48

1,2-Dichloropropane	4.16	92.75	1,2-Dibromo-3-chloroprop	5.40	83.03
methyl methacrylate	4.36	93.03	1,2,4-Trichlorobenzene	3.99	94.51
propyl acetate	4.30	92.32	Naphthalene	3.85	89.37
Dibromomethane	4.19	101.84	Hexachlorobutadiene	6.15	96.75
Bromodichloromethane	4.17	94.46	1,2,3-Trichlorobenzene	3.79	94.25

Table 7: Precision and Accuracy over Seven Days Data Summary

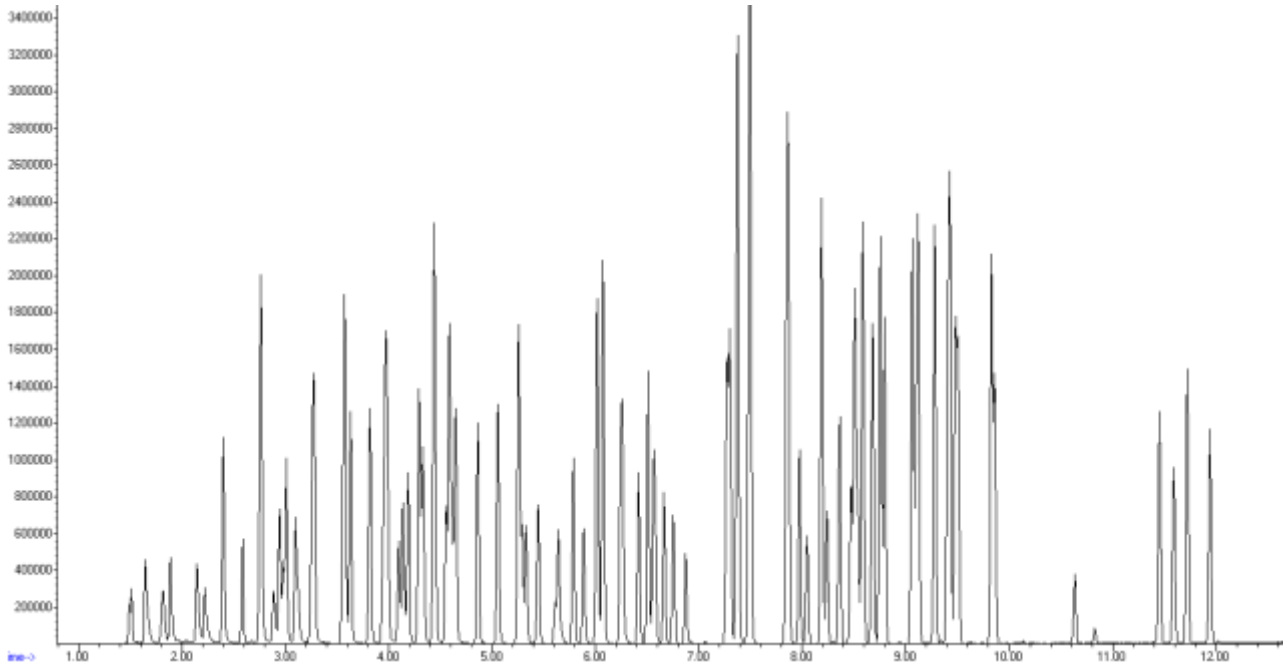

Figure 3: 46.5µg/L Chromatogram

CONCLUSIONS:

The ePrep proved to be an excellent option for the automation of volatile standard preparation. The calibration curve met all of the USEPA Method 8260D method requirements. Furthermore, that precision and accuracy of the samples displayed remarkable stability and reproducibility over the course of seven days. Automating volatile standard preparation would be invaluable to environmental labs as it would save time, remove errors and optimize lab personnel time and productivity.

REFERENCES:

1. Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); United States Environmental Protection Agency Method 8260D, Revision 4, February 2017.
2. Kuselman, Ilya, & Pennecchi, Francesca & Fajgelj, Ales & Karpov, Yury, (2013) "Human errors and reliability of test results in analytical chemistry, Accreditation and Quality Assurance. 18. 3-9.10.1007/s00769-012-0934-y.

...more about ePrep

The ePrep Sample Preparation Workstation utilises a suite of innovative technologies to bring automation of sample preparation to every analytical chemistry laboratory.

The ePrep can be programmed and operated by unskilled laboratory staff for the preparation of samples and external standards for analytical analysis. This significantly reduces errors, improves reproducibility, improves analysis cost and time

Its independent operation allows flexibility and effectiveness in a laboratory setting. Samples can be prepared in Autosampler Racks, away from analytical instrumentation.

...more about EST Purge and Trap

Evolution Purge and Trap Concentrator
The Evolution Purge and Trap concentrator offers unparalleled moisture control resulting in the most stable system available today. This capability means the Evolution can be run at lower split ratios, offering more sensitivity, less maintenance, and superior chromatographic resolution.

Centurion Purge and Trap Autosampler
The Centurion, the world's best-selling purge and trap Autosampler, is available in two models: water only (W) and a water/soil (WS) version. Offering 100 sample positions (90 positions for soil) in two 50-position removable trays, the Centurion platform is based on a well-proven, robust and state-of-the-art XYZ design. Automatic programmable internal standard addition with <3% RSD, low carryover, dilution capability up to 400:1 and overall reliability set the Centurion apart from the competition.

FOR MORE INFORMATION

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