Automated Standard Preparation for USEPA Method 8260D

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ABSTRACT

The preparation of Volatile Organic Standards (VOCs) for the United States Environmental Protection Agency (USEPA) Method 8260D 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.

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". This can result in lost time, wasted labor, 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 milliliter vials with no headspace. The ePrep sample preparation workstation 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 EST Analytical ePrep sample preparation workstation automated all of the sample preparation for USEPA Method 8260D. The EST Analytical Evolution and Centurion 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.

Table 1: ePrep Workflow for 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)	NA	NA	NA	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)	NA	NA	NA	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)	NA	NA	NA	2 mg/L standard

*NA - Not Applicable

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Table 2: ePrep Workflow for Calibration Standards

Step	Volume	Tool Wash Aspirate Flow-rate	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

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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.

Table : ePrep Workflow for Calibration Standards

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: Evolution and Centurion WS Experimental Parameters

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

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 1 is a display of the 46.5µg/L chromatogram.

Table 3: ePrep Workflow for Calibration Standards

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

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

CONCLUSIONS:

The instrument configuration and operating conditions listed and described above created impressive performance results for USEPA Method 624.1. All quality control criterions were met or exceeded for this updated method. The EST Analytical Evolution Purge and Trap concentrator and Centurion WS sampling system presented a number of unique features and benefits. For example the eight port valve in the concentrator eliminates the need to desorb through the moisture retention trap, thus limiting the water exposure to the GC. Furthermore, carryover was reduced using the patented feature of heating the sparge vessel during the trap bake cycle. These elements combined make the Evolution Purge and Trap and Centurion WS a superb addition to your environmental lab