Análisis de Compuestos VOC en aguas mediante EPA Método 8260 (PTC)

Aplicación 004 *By: Teri Dattilio*

Introduction

El método de concentración purga y trampa (P&T) asociado al análisis mediante cromatografía de gases (GC) es un método muy aceptado en la determinación de Compuestos Orgánicos Volátiles (VOC). Esta metodología fue desarrollada para alcanzar la sensibilidad necesaria en el análisis de VOC en aguas potables y otras matrices mediante la metodología (USEPA) Method 8260, 524.2, 502.2, 601, 602 etc.

Para cumplir las exigencias USEPA Method 8260, Teledyne Tekmar ha mejorado la tecnología P&T mediante el desarrollo sucesivo de nuevas generaciones de sistemas que mejoran su capacidad de concentración. El modelo Stratum PTC ofrecía una nueva trampa analítica con forma de " U " generando mejoras significativas frente a sus predecesores. El modelo LUMIN actual la mantiene pero mejora todavía más esta capacidad, Teledyne Tekmar ha desarrollado una trampa propia #9 que mejora la eficacia analítica de los compuestos más volátiles que se encuentran en las metodologías analíticas mencionadas.

En esta aplicación el análisis de agua se ejecuta con una calibración lineal y demuestra que 95 analitos son detectables en el rango de 0.5-200ppb. El Sistema utiliza un volumen de purga de 5 mls. Y las condiciones y parámetros analíticos reflejados en USEPA Method 8260. El modelo Stratum PTC y Aquatek 100 junto a un GC-MS Agilent 6890 GC and 5973 MSD son una herramienta excelente para el análisis de VOC presentes en agua.

Experimental-Instrument Conditions

An Agilent 6890/5973 GCMS, Stratum Purge and Trap Concentrator and Solatek 72 Multimatrix Autosampler were used for this analysis. Results and findings were obtained through the use of a 20m X 0.18mm X 1.0µm RTX-VMS fused silica capillary column (Restek Corporation). The Mass Spectrometer Detector (MSD) scanned in the full scan mode from 35-350m/z at 5.27 scan/sec. The GC, MSD and Purge and Trap conditions are shown in Tables 1, 2 and 3 respectively.

GC Parameters	
GC:	Agilent 6890
Column:	Restek RTX-VMS, 20m, 0
Oven Program:	35°C for 4 min.; 16°C/min 30°C /min to 210 °C for 3 min 1
Inlet:	150°C
Column Flow:	1.2 mL/min.
Gas:	Helium
Split:	30:1
Flow:	1.2mL/min
Pressure:	20psi

MSD Parameters	
MSD:	Agilent 5973
Source:	230°C
Quad:	150°C
Solvent Delay:	0.5 min
Column Flow:	1.2mL/min.
Scan Range:	mz 35-350
Scans:	5.27 scans/sec
Threshold:	400

Table 1 & 2: GC and MSD Parameters

Stratum PTC and Solatek 72 Parameters			
Variable	**Value**	**Variable**	**Value**
Rinse Water Temp	90°C	Sample Preheat Time	1.00 min
Sample Cup Temp:	30°C	Sample Temp	40°C
Sample Needle Temp	30°C	Purge Time	11.00
Transfer Line Temp	125°C	Purge Temp	0°C
Soil Valve Temp	125°C	Purge Flow	40 mL/min
Sample Sweep Time	0.50 min	Dry Purge Time	3.00 min
Needle Rinse Volume	7mL	Dry Purge Temp	20°C
Needle Sweep Time	0.50 min	Dry Purge Flow	100 mL/min
Bake Rinse Volume	7mL	GC Start	Start of Desorb
Bake Sweep Time	0.25 min	Desorb Preheat Temp	245°C
Bake Drain Time	0.50 min	Desorb Drain	On
Number of Bake Rinses	3	Desorb Time	2.00 min
Valve Oven Temp	150°C	Desorb Temp	250°C
Transfer Line Temp	150°C	Desorb Flow	300mL/min
Sample Mount Temp	90°C	Bake Time	4.00 min
Purge ready Temp	40°C	Bake Temp	250°C
Condenser Ready Temp	45°C	Bake Flow	400mL/min
Condenser Purge Temp	20°C	Condenser Bake Temp	200°C
Standby Flow	25mL/min	Focus Temp	-150°C
Pre-Purge Time	0.00 min	Inject Temp	180°C
Pre-Purge Flow	40mL/min	Inject Time	1.00 min
Sample Heater	Off	Standby Temp	100°C

Table 3: Stratum PTC/Solatek 72 Parameters

Stratum PTC Parameters are Indicated in blue

Calibration

A working standard was prepared in methanol at a final standard concentration of 50ppm. Calibration standards were prepared in 100mL volumetric flasks filled to volume with deionized water over the calibration range of 0.5200ppb and transferred headspace free directly to VOA vials for analysis. Internal Standards (IS) were added at
5µLusing the Internal Standards Addition Module of the Solatek 72 Autosampler to hold at a constant concentration of 25ppb. Sample volume was a 5mL aliquot using the instrument conditions mentioned previously.

Calibration data was processed using Agilent ChemStation software. All analytes and their corresponding calibration data were evaluated using both the %RSD of the relative response factor and by calibration curve linearity. For most compounds the %RSD was <12% over the entire 0.5-200ppb calibration range. For those target compounds with %RSD >15%, linear regression was employed with acceptance at 0.995 or greater, indicating linear response for all target analytes. The calibration data meets all USEPA Method 8260 performance criteria. Calibration data, along with results of a 50ppb Continuing Calibration Verification (CCV) standard are presented in Table 4. Figure 1 shows the total ion chromatogram of a 25ppb standard.

Method Detection Limit (MDL) Determination

A study was performed to statistically determine the Method Detection Limits (MDL's) according to the procedure in USEPA Method 8260. Seven aliquots of a 1.0ppb standard were analyzed and the data processed to determine the MDL's for the compounds listed in Table 4. The detection limit results for most of the compounds were 0.5 µg/L or less. The data collected met system performance criteria for Method 8260.

MDL according to 40CFR 136, Appendix B, Revision 1.11					
Compound	Spike level (ug/L)	%RSD	MDL	50ppb CCV (%DEV)	%Carryover
Pentafluorobenzene (IS)	25.0		0.000	0.00	
Dichlorodifluoromethane	1.00	7.84	0.310	109	0.05
Chloromethane	1.00	7.09	0.387	105	0.13
Vinyl Chloride	1.00	9.92	0.490	110	0.14
Bromomethane	1.00	7.46	0.081	100	0.29
Chloroethane (Ethyl Chloride)	1.00	12.42	0.439	101	0
Trichlorofluoromethane	1.00	11.08	0.543	106	0.02
Diethyl Ether	1.00	9.39	0.302	108	0
1,1-Dichloroethene	1.00	14.54	0.227	112	0
Carbon Disulfide	1.00	11.34	0.246	98	0.21
1,1,2-Trichlorofluoroethane	1.00	12.94	0.294	102	0.03
Iodomethane	1.00	8.38	0.616	137	0.25
Allyl Chloride	1.00	10.59	0.405	91	0.15
Methylene Chloride	1.00	8.70	0.510	97	0.06
Acetone	1.00	8.50	0.548	114	0.11
trans-1,2-Dichloroethene	1.00	10.81	0.199	103	0.22
Methyl Acetate	1.00	13.05	0.386	106	0.14
MTBE	1.00	7.56	0.365	106	0.01
TBA	1.00	10.10	0.237	104	0.02
Diisopropyl Ether	1.00	12.33	0.344	103	0.22
Chloroprene	1.00	7.71	0.318	104	0.14
1,1-Dichloroethane	1.00	10.14	0.325	101	0.02
Acrylonitrile	1.00	10.62	0.222	102	0.04
Vinyl acetate	1.00	11.67	0.600	103	0.02
ETBE	1.00	7.32	0.257	102	0

cis-1,2-Dichloroethene	1.00	6.95	0.378	100	0.18
2,2-Dichloropropane	1.00	13.70	0.529	102	0.00
Bromochloromethane	1.00	8.47	0.359	96	0.06
Chloroform	1.00	8.48	0.357	96	0.14
Carbon Tetrachloride	1.00	6.02	0.504	105	0.03
1,1,1-Trichloroethane	1.00	11.65	0.342	96	0
THF	1.00	7.40	0.459	102	0
Dibromofluoromethane (Surr)	1.00	8.95	0.318	98	0.03
Methyl Acrylate	1.00	6.30	0.358	105	0.05
1,1-Dichloropropene	1.00	10.33	0.408	97	0.24
2-Butanone (MEK)	1.00	13.57	0.416	97	0
Benzene	1.00	9.29	0.337	97	0.09
Propionitrile	1.00	9.58	0.297	102	0
tert Amyl Methyl Ether	1.00	12.09	0.242	97	0.00
($_1^{TAME}$,2-Dichloroethane)	1.00	11.67	0.322	94	0.00
Isobutyl Alcohol	1.00	0.9985	0.375	90	0.09
Isopropyl Acetate	1.00	10.36	0.337	111	0
Trichloroethene	1.00	8.12	0.478	116	0.08
1,4-Difluorobenzene (IS)	25.00		0.000		
Dibromomethane	1.00	10.18	0.302	95	0.11
1,2-Dichloropropane	1.00	7.22	0.405	96	0
Bromodichloromethane	1.00	10.42	0.306	92	0.04
Methyl Methacrylate	1.00	0.9991	0.375	87	0.02
n-Propyl Acetate	1.00	0.9995	0.360	87	0.01

Stratum y LUMIN PTC Purge and Trap Concentrator

Aquatek 100

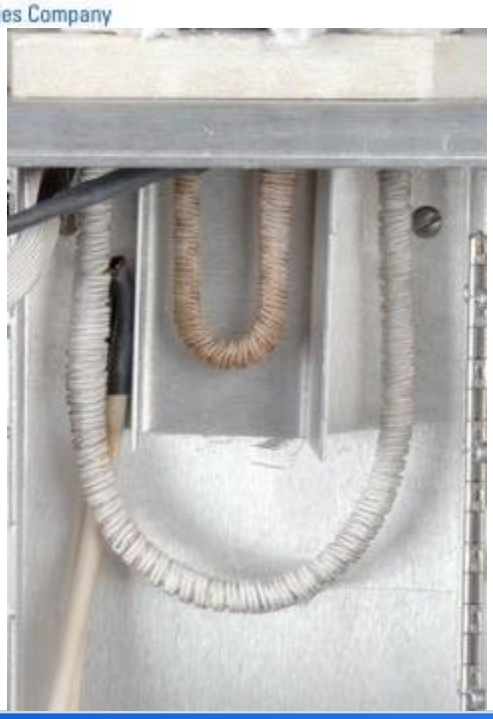
TELEDYNE INSTRUMENTS
Tekmar
A Teledyne Technologies Company

innovación tecnológica para laboratorio Rafer

Stratum PTC Newly Designed Ushaped Analytical and Condensate Traps

MDL according to 40CFR 136, Appendix B, Revision 1.11					
Compound	Spike level (ug/L)	%RSD	MDL	50ppb CCV (%DEV)	%Carryover
2-Cleve	1.00	0.9999	0.297	86	0.02
cis-1,3-Dichloropropene	1.00	14.47	0.304	113	0.07
Toluene-d8 (surr)	1.00	13.50	0.316	112	0.07
Toluene	1.00	11.96	0.277	112	0.08
Tetrachloroethene	1.00	5.77	0.653	103	0.07
4-methyl2-pentanone	1.00	0.9999	0.260	98	0.02
1,1,2-Trichloroethane	1.00	7.56	0.371	96	0.02
Ethyl Methacrylate	1.00	0.9999	0.277	83	0
Dibromochloromethane	1.00	11.84	0.592	96	0.02
1,3-Dichloropropane	1.00	5.11	0.376	101	0.04
1,2-Dibromoethane	1.00	6.35	0.296	97	0.10
n-Butyl Acetate	1.00	11.23	0.316	105	0.02
2-Hexanone	1.00	11.42	0.448	109	0.02
Chlorobenzene-d5 (IS)	25.00		0.000		
Chlorobenzene	1.00	9.11	0.357	94	0.18
Ethylbenzene	1.00	6.32	0.490	104	0.10
1,1,1,2-Tetrachloroethane	1.00	13.61	0.329	90	0.00
M&P Xylene	1.00	9.80	0.571	112	0.06
Ortho Xylene	1.00	13.23	0.517	113	0.04
Styrene	1.00	14.12	0.493	112	0.07
Bromoform	1.00	7.82	0.274	99	0.03
Isopropylbenzene	1.00	0.9976	0.346	109	0.05
n-Amyl Acetate	1.00	0.9994	0.367	100	0.00
BFB (surr)	1.00	6.17	0.389	103	0.12
n-Propylbenzene	1.00	12.75	0.473	111	0.09
cis-1,4-Dichloro-2-Butene	1.00	6.24	0.447	102	0.04
Bromobenzene	1.00	10.38	0.412	97	0.14
1,1,2,2-Tetrachloroethane	1.00	10.74	0.424	89	0.04
1,3,5-Trimethylbenzene	1.00	12.86	0.424	115	0.06
2-Chlorotoluene	1.00	9.88	0.436	106	0.08
trans-1,4-Dichloro-2-Butene	1.00	8.34	0.473	102	0.04
4-Chlorotoluene	1.00	8.01	0.374	108	0.12
Tertbutylbenzene	1.00	12.55	0.661	110	0.08
1,2,4-Trimethylbenzene	1.00	14.06	0.551	113	0.05
sec-Butylbenzene	1.00	12.81	0.425	111	0.07
p-Isopropyltoluene	1.00	0.9986	0.423	108	0.06
1,3-Dichlorobenzene	1.00	5.85	0.374	95	0.22
1,4-Dichlorobenzene-d4 (IS)	25.00		0.000		
1,4-Dichlorobenzene	1.00	14.08	0.382	89	0.32
n-Butylbenzene	1.00	9.23	0.478	108	0.15
1,2-Dichlorobenzen	1.00	6.40	0.373	95	0.05
1,2-Dibromo-3-Chloropropane	1.00	13.60	0.222	95	0
Nitrobenzene	1.00	0.9959	0.282	90	0.06
Hexachlorobutadiene	1.00	13.03	0.253	92	0.21
1,2,4-Trichlorobenzene	1.00	12.24	0.480	103	0.21
Naphthalene	1.00	13.97	0.702	112	0.11
1,2,3-Trichlorobenzene	1.00	11.84	0.465	99	0.19

Table 4: Calibration %RSDs and Statistically Determined Method Detection Limits for 8260 Target Compounds



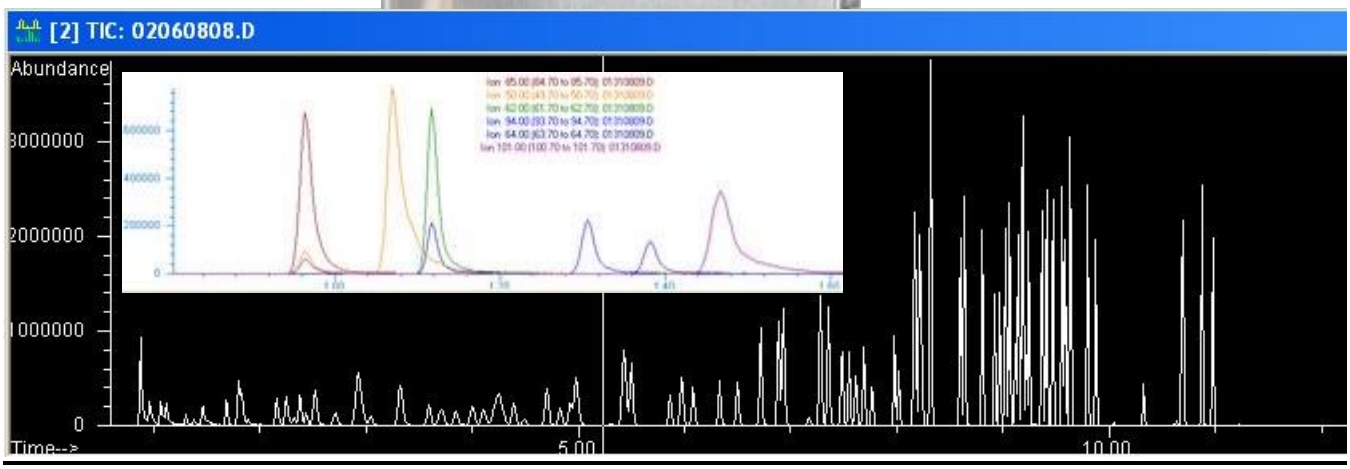


Figure 1: Total Ion Chromatogram of a 25ppb Calibration Standard

Carryover Evaluation

Data was collected and evaluated for carryover of target analytes in subsequent blanks following a 200ppb calibration standard. The Stratum PTC and Solatek 72 Multimatrix Autosampler performed remarkably well indicating <0.4% carryover in the first blank for all 95-target analytes evaluated. This data is also presented in Table 4.

Conclusion

The need for water removal from Purge and Trap analysis has been present since the introduction of Purge and Trap technology. The Stratum PTC is equipped with an innovative U-shaped condensate trap. The unique geometry of the trap aids in the removal of water that is typical in Purge and Trap analysis. The new condensate trap offers improved water management and therefore a great replacement to early generation concentrators. Increasing demands for low-level sensitivity for VOC analysis has led the need for improved Purge and Trap technology. The new proprietary Tekmar #9 analytical trap performs well on troublesome early eluting compounds as well as difficult to retain compounds like 2-chlorovinyl ether and nitrobenzene. Using the # 9 trap, analysis of volatile organic compounds by USEPA Method 8260 was demonstrated. Linear calibration was also demonstrated over the range of 0.5-200ppb for 95 target compounds. USEPA Method 524.2 has similar requirements and target compounds which overlap those performed in this application. The new Siltek coated

sample pathway proves to be the optimal choice for sample inertness for pathway sensitive compounds such as halogenates and others. Previous problems associated with carryover in Purge and Trap analysis have been addressed by reducing the sample pathway and a more uniform heating design. The new Stratum PTC and Solatek 72 Multimatrix Autosampler prove to be excellent analytical instruments. Teledyne Tekmar once again continues to offer excellent water management, improved analytical performance and a reduction in carryover in subsequent samples all while satisfying the requirements of multiple EPA and other analytical methods.