Chromatography
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US EPA Method 624.1 with the Tekmar Lumin P&T and the Thermo Scientific™ TRACE™ 1610 GC and ISQ™ 7610 MS System with an HeSaver-H₂Safer™ SSL Injector and an ExtractaBrite Source

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Abstract

As helium supplies become scarcer and more expensive, customers have been seeking alternative carrier gases or ways to conserve helium without sacrificing system performance. This analysis will evaluate the Teledyne LABS Tekmar Lumin Purge and Trap (P&T) concentrator along with the AQUATek LVA autosampler in conjunction with a Thermo Scientific TRACE 1610 Gas Chromatograph (GC) equipped with the HeSaver-H₂Safer™ SSL injector and the ISQ 7610 Mass Spectrometer (MS) with an ExtractaBrite source performing US EPA Method 624.1 to determine the concentration of Volatile Organic Compounds (VOCs) in wastewater matrices. Using nitrogen as the purge gas, along with the HeSaver-H₂Safer™ SSL injector, significantly reduces helium gas consumption during analysis without sacrificing system performance. The method was validated by a working relative standard deviation (%RSD) calibration curve, method detection limits (MDL), and a mid-point calibration check with accuracy and precision.

Introduction

The Tekmar Lumin P&T has an innovative moisture control system (MCS) that improves water vapor removal by as much as 60%, thereby reducing peak interference and increasing GC column lifespan. The AQUATek LVA autosampler has an 84-position chiller enabled sample tray and utilizes a fixed volume loop that transfers the liquid sample, internal standards, and surrogate standards to the Lumin P&T concentrator. In addition to other refinements, the AQUATek LVA incorporates a precision-machined valve manifold block to reduce potential leak sources and ensure the system is both reliable and robust

Sample Preparation

A 50 parts per million (ppm) calibration working standard was prepared in methanol from the following Restek® standards: 624.1 Calibration Mix #1 Gases and EPA Method 624.1 Volatiles MegaMix Standard. In total, the standards contained 31 compounds.

A seven-point calibration curve was prepared from 0.5 ppb to 100 parts per billion (ppb) for all compounds with relative standard deviation (%RSD) <35%. The average response factor (RF) was calculated for each compound using three internal standards: bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane. Surrogate standards consisted of pentafluorobenzene, fluorobenzene, and 1-bromo-4-fluorobenzene. Internal and surrogate standards were prepared in methanol from Restek standards at a concentration of 25 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 25 ppb.

Seven 0.5 ppb standards were prepared to calculate the MDL and precision calculations. Also, seven 20 ppb standards were prepared for the accuracy and precision calculations of the mid-point calibration check. All calibration, MDL, and mid-point calibration check standards were analyzed with the Tekmar Lumin P&T and AQUATek LVA conditions in Table I. GC-MS conditions are shown in Table II.

Experimental Instrument Conditions

Table I Tekmar Lumin P&T and AQUATek LVA Water Method Conditions

Standby	Variable	Desorb	Variable
Valve Oven Temp	140 °C	Desorb Preheat Temp	245 °C
Transfer Line Temp	140 °C	Desorb Temp	250 °C
Sample Mount Temp	90 °C	Desorb Time	1.00 min
Standby Flow	10 mL/min	Drain Flow	300 mL/min
Purge Ready Temp	35 °C	GC Start Signal	Begin Desorb
MCS Purge Temp	20 °C	**Bake**	**Variable**
Purge	**Variable**	Bake Time	3.00 min
Purge Temp	20 °C	Bake Temp	270 °C
Purge Time	8.00 min	MCS Bake Temp	180 °C
Purge Flow	50 mL/min	Bake Flow	200 mL/min
Dry Purge Temp	20 °C	**AQUATek LVA**	**Variable**
Dry Purge Time	1.00 min	Sample Loop Time	0.35 min
Dry Purge Flow	100 mL/min	Sample Transfer Time	0.35 min
Sparge Vessel Heater	Off	Rinse Loop Time	0.30 min
		Sweep Needle Time	0.30 min
		Presweep Time	0.25 min
Trap	9	Water Temp	90 °C
Chiller Tray	Off	Bake Rinse Cycles	1
Purge Gas	Nitrogen	Bake Rinse Drain Time	0.35 min

Table II Thermo Scientific TRACE 1610 GC and ISQ 7610 MS System Conditions

Thermo Scientific TRACE 1610 GC Conditions	
Column	TG-VMS, 30 m x 0.25 mm, 1.4µm Film, Column Flow, Helium – 1.5 mL/min
Oven Profile	35 °C, 2 min, 15 °C/min to 100 °C, 30 °C/min to 225 °C, 1 min Hold, Run Time 12.5 min
Inlet	200 °C, 30:1 Split, Purge Flow 5.0 mL/min, 0.40 min Helium Delay
Thermo Scientific ISQ 7610 MS Conditions	
Temp	Transfer Line 230 °C; Ion Source 280 °C
Scan	Range 35 *m/z* to 260 *m/z*, Solvent Delay 1.54 min, Dwell/Scan Time 0.10 sec
Current	Emission Current 25 µA, Gain 3.00E+005

Results

The relative standard deviation (%RSD) calibration curve, MDL, and mid-point calibration check data are shown in Table III. Figure 1 displays a 20 ppb calibration standard, with an inset demonstrating excellent peak shape and separation across all concentrations with minimal water interference for all target compounds.

Table III **US EPA Method 624.1 Calibration, MDL, and Mid-point Check**

Compound	Calibration (0.5-100 ppb)				Method Detection Limit (n=7, 0.5 ppb)		Mid-point Check (n=7, 20 ppb)	
	Ret. Time	Confirm. Ion	Relative SD (<35%RSD)	Avg. RF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±20%)
Chloromethane	1.65	50	3.0	2.58	0.07	4.7	4.4	93
Vinyl Chloride	1.72	62	6.0	1.43	0.05	3.0	4.0	86
Bromomethane	2.01	94	5.4	1.09	0.11	6.7	2.6	88
Chloroethane	2.14	64	5.5	1.23	0.13	9.2	2.7	81
Trichlorofluoromethane	2.27	101	4.9	2.05	0.08	5.4	3.8	88
1,1-Dichloroethene	2.74	61	4.2	0.699	0.11	7.6	4.2	87
Methylene Chloride	3.25	84	6.9	0.830	0.12	7.5	2.7	87
trans-1,2-Dichloroethene	3.39	61	6.7	0.689	0.13	8.5	3.9	88
1,1-Dichloroethane	3.90	63	6.0	1.94	0.09	5.7	1.8	91
Bromochloromethane (IS)	4.48	49						
Chloroform	4.55	83	9.6	1.23	0.06	3.5	1.7	92
Carbon Tetrachloride	4.65	117	7.7	0.613	0.07	4.3	2.8	91
1,1,1-Trichloroehane	4.70	97	9.2	0.857	0.12	7.1	2.2	92
Benzene	4.99	78	7.6	2.01	0.05	3.3	2.0	92
Pentafluorobenzene (SURR)	5.06	168	3.1	2.36		1.3	1.4	100
1,2-Dichloroethane	5.16	62	10.0	0.774	0.06	3.5	1.2	92
Fluorobenzene (SURR)	5.32	96	6.4	2.33		1.3	1.5	99
Trichloroethylene	5.45	130	10.3	0.564	0.10	5.5	1.5	94
1,2-Dichloropropane	5.87	63	8.3	0.728	0.08	5.1	1.7	91
Bromodichloromethane	5.92	83	7.4	0.952	0.05	3.0	1.6	94
2-Chloroethyl Vinyl Ether	6.38	63	7.5	0.469	0.10	6.6	1.6	93
Toluene	6.61	91	11.1	2.26	0.09	5.8	2.1	90
Tetrachloroethylene	6.89	164	10.7	0.461	0.10	6.0	2.3	91
cis-1,3-Dichloropropene	6.91	75	8.2	1.07	0.09	3.2	1.5	93

Table III **US EPA Method 624.1 Calibration, MDL, and Mid-point Check**

Compound	Calibration (0.5-100 ppb)				Method Detection Limit (n=7, 0.5 ppb)		Mid-point Check (n=7, 20 ppb)	
	Ret. Time	Confirm. Ion	Relative SD (<35%RSD)	Avg. RF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±20%)
2-Bromo-1-Chloropropane (IS)	6.92	77						
1,1,2-Trichloroethane	7.03	97	4.1	0.566	0.06	3.9	1.6	94
Dibromochloromethane	7.15	127	6.9	0.468	0.04	2.6	2.0	94
Chlorobenzene	7.68	112	6.3	1.38	0.06	3.7	3.0	94
trans-1,3-Dichloropropene	7.68	77	5.9	1.05	0.06	3.5	3.4	92
Ethylbenzene	7.69	106	6.2	0.735	0.05	3.5	3.9	96
Bromoform	8.12	173	9.3	0.504	0.08	5.7	2.2	95
4-Bromofluorobenzene (SURR)	8.45	95	1.2	0.828		0.8	1.1	103
1,4-Dichlorobutane (IS)	8.55	55						
1,1,2,2-Tetrachloroethane	8.58	83	3.9	0.809	0.08	5.9	1.7	91
1,3-Dichlorobenzene	9.09	146	4.2	1.78	0.06	3.5	2.7	100
1,4-Dichlorobenzene	9.14	146	4.7	1.84	0.07	4.0	2.9	100
1,2-Dichlorobenzene	9.39	146	5.0	1.82	0.05	2.9	2.7	102

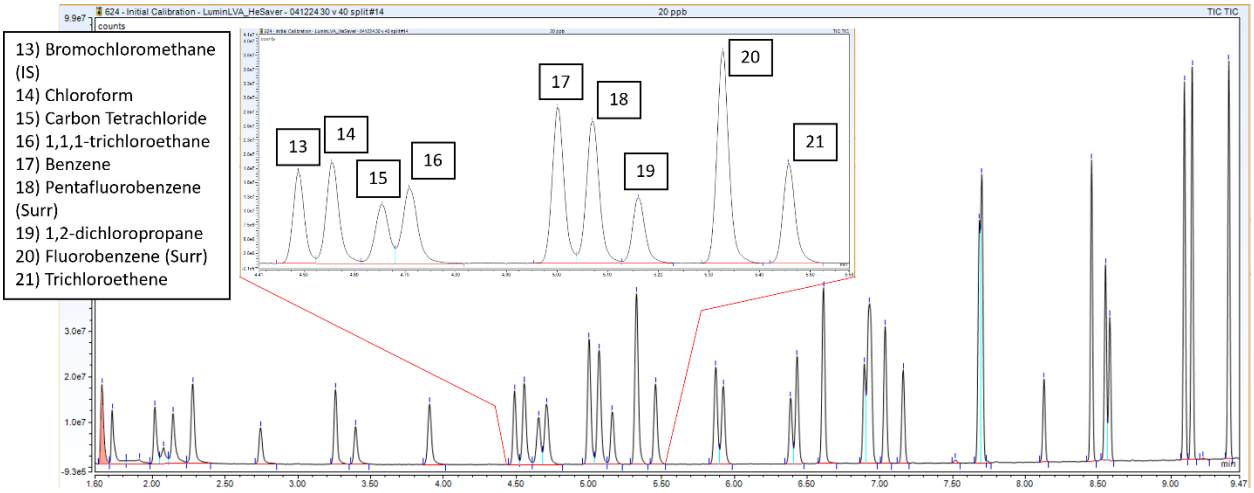

Figure 1 Total ion chromatogram (TIC) of US EPA method 624.1 20 ppb calibration standard, with an inset demonstrating excellent peak shape and separation across all concentrations with minimal water interference for all target compounds.

Conclusion

This study demonstrates the capability of the Tekmar Lumin P&T and AQUATek LVA system to process VOCs in wastewater samples following the US EPA Method 624.1 with detection by an Thermo Scientific TRACE 1610 GC and the ISQ 7610 MS. Utilizing the Lumin P&T's ability to purge with nitrogen, along with using Thermo's HeSaver-H_2Safer™ SSL injector, helium was conserved during this analysis without sacrificing system performance. The relative standard deviation (%RSD) of the calibration curve from 0.5 ppb to 100 ppb passed method requirements. Furthermore, the average MDL for all compounds was 0.08 ppb with a 4.6% RSD. Seven 20 ppb mid-point calibration check standards averaged a 93% recovery with a 2.4% RSD.

References

1. U.S. Environmental Protection Agency; Method 624.1 – Purgeables by GC/MS; December 2014.