APPLICATION NOTE: AN2106
TECHNOLOGY: P+T VOC
INDUSTRY: ENV

Italian Legislative Decree 152/2006 Using the Tekmar Lumin P&T Concentrator, AQUATek LVA and Thermo Scientific™ TRACE™ 1310 GC and ISQ™ 7000 MS with an Advanced Electron Ionization (AEI) Source

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Abstract

Italian Legislative Decree 152/2006 was used to determine the concentration of volatile organic compounds (VOCs) in water matrices. The Teledyne Tekmar Lumin purge and trap (P&T) concentrator in combination with an AQUATek LVA liquid autosampler and a Thermo Scientific TRACE 1310 Gas Chromatograph (GC)/ISQ 7000 Mass Spectrometer (MS) with an Advanced Electron Ionization (AEI) source was used to create a working linear calibration curve and method detection limits (MDLs) for target compounds. This study will demonstrate the ability of the Lumin P&T concentrator's innovative moisture control system (MCS) to remove water vapor transferred to the GC/MS.

Introduction

The AQUATek LVA is Teledyne Tekmar's most advanced P&T system and is based on the proven Atomx XYZ platform. The AQUATek LVA includes whisper quiet XYZ automation, dual standard addition vessels and an optional pH meter. Combined with its 84-position chiller enabled sample tray, the result is more reliable sample preparation and handling. When combined with a Lumin PTC, an innovative moisture control system (MCS) improves water vapor removal by as much as 60%, thereby reducing peak interference and increasing GC column life span. 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 10-ppm working calibration standard mix was prepared together in methanol from Restek® standards using Drinking Water VOA MegaMix™ and 502.2 Calibration Mix. In total, the standards contained 43 compounds.

A water calibration curve was prepared from 0.1 ppb (100 ppt) to 1.1 ppb (1100 ppt) for all compounds. The relative response factor (RF) was calculated for each compound using one internal standard: Fluorobenzene. Surrogate standards consisted of: 4-Bromofluorobenzene and 1,2-Dichlorobenzene-d4. Internal Standards and Surrogates were prepared together in methanol from Restek at a concentration of 5 ppm, with 5 µL mixed with each 5 mL sample for a resulting concentration of 5 ppb.

Seven 0.1 ppb (100 ppt) standards were prepared for method detection limit (MDL), accuracy and precision calculations. All calibration and MDL samples were analyzed with the Teledyne Tekmar Lumin P&T concentrator and AQUATek LVA conditions in Table I and the GC/MS conditions in Table II.

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Experimental Instrument Conditions

Table I Teledyne Tekmar Lumin P&T Concentrator/AQUATek LVA Water Method Conditions			
Standby	**Variable**	**Desorb**	**Variable**
Valve Oven Temp	150 ºC	Desorb Preheat Temp	245 ºC
Transfer Line Temp	150 ºC	Desorb Temp	250 ºC
Sample Mount Temp	90 ºC	Desorb Time	2.00 min
Standby Flow	10 mL/min	Drain Flow	300 mL/min
Purge Ready Temp	35 ºC	GC Start Signal	Start Only
MCS Purge Temp	20 ºC		
Purge	**Variable**	**Bake**	**Variable**
Purge Temp	20 ºC	Bake Time	2.00 min
Purge Time	11.00 min	Bake Temp	280 ºC
Purge Flow	40 mL/min	MCS Bake Temp	180 ºC
Dry Purge Temp	20 ºC	Bake Flow	200 mL/min
Dry Purge Time	1.00 min		
Dry Purge Flow	100 mL/min	**AQUATek LVA**	**Variable**
Sample Heater Enable	Disabled	Sample Loop Time	0.35 min
Sample Temp		Sample Transfer Time	0.35 min
Pre-Purge Time		Rinse Loop Time	0.30 min
Pre-Purge Flow		Sweep Needle Time	0.30 min
Preheat Time		Presweep Time	0.25 min
Trap	9	Water Temp	90 ºC
Chiller Tray	Off	Bake Rinse Cycles	1
Purge Gas	Nitrogen	Bake Rinse Drain Time	0.35 min

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Table II Thermo Scientific TRACE 1310 GC and ISQ 7000 MS System Conditions	
Thermo Scientific TRACE 1310 GC Conditions	
Column	Rtx® VMS, 20 m x 0.18 mm, 1µm Film, Helium – 0.8 mL/min
Oven Profile	35 ºC, 2 min, 12 ºC/min to 85 ºC, 20ºC/min to 225 ºC, 2 min Hold, Run Time 15.167 min
Inlet	200 ºC, Split flow: 48 mL/min, 60:1 Split, Purge Flow: 0.5 mL/min
Thermo Scientific ISQ 7000 MS Conditions	
Temp	Transfer Line 230 ºC; Ion Source 300 ºC
Sim Ions	Full Scan – Mass Range 35-260 amu, Solvent Delay 0.50 min, Dwell/Scan Time: 0.1 sec
Current	Emission Current 50 µA, Gain 5.00E+006

Results

The relative standard deviation (%RSD) of the RFs for the calibration curve, MDL, accuracy, and precision data are shown in Table III. Figure 1 displays a 0.6 ppb (600 ppt) standard, indicating excellent peak resolution for VOC standards.

Table III Italian Legislative Decree 152/2006 Calibration, Accuracy and Precision Data

Compound	Calibration				Accuracy and Precision (n=7, 0.1 ppb)[1]		
	Retention Time	Linearity RF (≤20%RSD)	MDL (ppb)	Average RF	Average Concentration (ppb)	Precision (≤20%RSD)	Accuracy (±20%)
Chloromethane	1.38	6.21	0.02	0.629	0.09	7.82	94
Vinyl Chloride	1.45	3.36	0.02	0.772	0.09	7.41	88
Chloroethane	1.83	4.44	0.03	0.516	0.09	11.5	92
1,1-Dichloroethene	2.37	2.37	0.03	3.35	0.11	10.0	107
Methylene Chloride	2.80	16.3	0.01	1.79	0.130	2.79	125
cis-1,2-Dichloroethene	2.91	1.43	0.03	1.70	0.09	11.0	86
Methyl tert-Butyl Ether	3.02	4.86	0.01	1.43	0.09	4.33	91
1,1-Dichloroethane	3.39	3.93	0.02	2.37	0.09	8.31	93
trans-1,2-Dichloroethene	3.80	2.75	0.01	1.09	0.09	5.01	85
Chloroform	4.04	4.64	0.01	1.40	0.09	5.22	86
Carbon Tetrachloride	4.12	5.46	0.01	0.743	0.08	5.01	78
1,1,1-Trichloroethane	4.18	3.74	0.02	0.920	0.09	6.87	85
Benzene	4.48	1.15	0.01	2.06	0.09	4.37	90
1,2-Dichloroethane	4.66	3.32	0.01	1.45	0.09	2.94	88
Fluorobenzene (IS)	4.83						
Trichloroethylene	4.97	11.3	0.04	0.643	0.11	10.1	114
1,2-Dichloropropane	5.42	2.18	0.02	0.735	0.09	5.97	90
Bromodichloromethane	5.49	2.43	0.01	0.897	0.09	4.31	87
cis-1,3-Dichloropropene	6.06	4.20	0.02	0.629	0.09	7.81	89
Toluene	6.27	2.72	0.01	1.84	0.09	4.36	91
Tetrachloroethene	6.60	5.34	0.01	0.749	0.09	5.03	90

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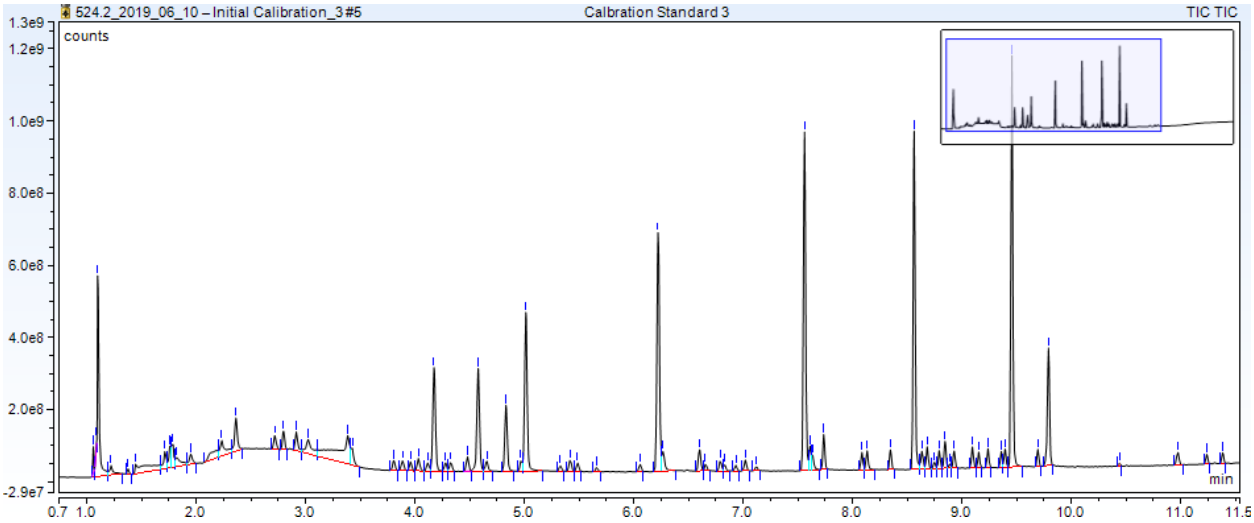
	Retention Time	Linearity RF (≤20%RSD)	MDL (ppb)	Average RF	Average Concentration (ppb)	Precision (≤20%RSD)	Accuracy (±20%)
trans-1,3-Dichloropropene	6.66	5.29	0.03	0.601	0.08	10.8	83
1,1,2-Trichloroethane	6.79	4.70	0.01	0.469	0.09	5.11	91
Dibromochloromethane	6.93	4.20	0.02	0.423	0.09	6.82	88
1,3-Dichloropropane	7.03	6.53	0.01	0.833	0.09	3.20	89
1,2-Dibromoethane	7.12	7.65	0.01	0.434	0.09	3.35	90
Chlorobenzene	7.58	2.48	0.02	1.21	0.09	6.11	91
Ethylbenzene	7.62	4.35	0.02	1.82	0.09	7.50	89
1,1,1,2-Tetrachloroethane	7.64	3.16	0.02	0.376	0.09	6.37	87
m, p-Xylene	7.74	2.96	0.04	0.604	0.19	6.30	94
o-Xylene	8.09	3.71	0.02	0.566	0.09	5.62	94
Bromoform	8.14	6.11	0.02	0.238	0.08	6.17	83
Styrene	8.14	4.21	0.01	0.839	0.09	5.26	85
4-Bromofluorobenzene (SURR)	8.57	3.36		2.16	5.03		101
1,1,2,2-Tetrachloroethane	8.75	3.71	0.02	0.418	0.08	7.64	82
2-Chlorotoluene	8.80	3.44	0.02	1.40	0.08	6.15	82
1,2,3-Trichloropropane	8.89	4.09	0.06	0.106	0.10	18.7	100
4-Chlorotoluene	8.93	7.36	0.01	1.30	0.08	5.25	83
1,3-Dichlorobenzene	9.40	4.94	0.02	0.783	0.09	8.16	85
1,4-Dichlorobenzene	9.79	3.78	0.02	0.345	0.09	5.51	91
1,2-Dichlorobenzene (SURR)	9.80	2.80		0.803	4.86		97
1,2-Dichlorobenzene	9.80	2.80	0.02	0.803	0.09	6.06	91
Hexachlorobutadiene	10.4	9.9	0.03	0.012	0.09	10.0	93
Nitrobenzene	10.97	6.74	0.05	0.147	0.09	17.6	94
1,2,4-Trichlorobenzene	10.99	5.28	0.02	0.315	0.09	7.73	93
1,2,3-Trichlorobenzene	11.39	7.54	0.01	0.339	0.09	3.91	94

1. Data from seven 0.1 ppb samples.

Figure 1 Total Ion Chromatogram of a Water Method 0.6 ppb (600 ppt) VOC Standard Indicating Consistent Peak Shapes for all Compounds and Minimal Water Interference.



Conclusion

This study demonstrates the capability of the Teledyne Tekmar Lumin P&T concentrator and AQUATek LVA liquid autosampler to process VOCs in water samples following Article 275 of Italian Legislative Decree 152/2006, Annex III Part 5, with detection by a Thermo Scientific TRACE 1310 Gas Chromatograph (GC)/ISQ 7000 Mass Spectrometer (MS) with an Advanced Electron Ionization (AEI) source. The %RSD of the calibration curve passed all method requirements. Furthermore, MDL, precision and accuracy for seven 0.1 ppb (100 ppt) standards showed minimal interference from excessive water.

By making additional, appropriate changes to the GC oven temperature program, the GC/MS cycle time may also be reduced, increasing laboratory throughput in a 12-hour period.

References

1. Italian Legislative Decree 152/2006, Annex III Part 5.