Application Note

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Italian Legislative Decree 152/2006 with the Teledyne Tekmar Lumin Purge and Trap Paired with the AQUATek LVA and Agilent GC/MS system

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Abstract

Italian Legislative Decree 152/2006 was used as a regulation metric for the concentration of volatile organic compounds (VOCs) in drinking water. The Teledyne Tekmar Lumin Purge and Trap (P&T) automated VOC sample preparation system was paired with the AQUATek LVA liquid vial autosampler and an Agilent 7890B GC and Agilent 5977A GC/MSD. Selective ion monitoring (SIM)/Scan mode was used to create a working linear regression (R^2) calibration curve, method detection limits (MDLs), and a midpoint calibration check for target compounds.

Introduction

Article 275 of Italian Legislative Decree 152/2006, Annex III Part 5 describes the regulations for VOCs in water, as well as method parameter limitations and guidelines. When conducting drinking water analyses, it is imperative to achieve high levels of accuracy and precision to protect public health and safety. Within these regulations of VOCs, two compounds have legal limits at the low level of one part per trillion (ppt) in water, with a detection limit at 0.1 ppt, one-tenth of the lower limit. These compounds include 1,2-dibromoethane and 1,2,3-trichloropropane, which have been identified as known or suspected human or mammalian carcinogens.

When performing drinking water analysis at such low levels, excess water vapor in the system can be a major concern. The water peak will minimize the sensitivity of the analysis, cause compounds to coelute or shift in retention time, and cause poor peak shape. The Teledyne Tekmar Lumin P&T has a moisture control system (MCS) that improves water vapor removal by as much as 60%, thereby reducing peak interference and increasing GC column lifespan.

Experimental

Sample preparation

A 50 parts per billion (ppb) working calibration standard was prepared in 1 mL of methanol from the two following Agilent standards: VOC liquids standard (part number DWM-524A-1) and VOC gas standard (part number DWM-544-1). A commercially available 1,2,4,5-tetrachlorobenzene standard was also used in the calibration standard.

A seven-point linear regression (R^2) calibration curve was prepared from 1 to 100 ppt for 1,2-dibromoethane and 1,2,3-trichloropropane in SIM mode. In full scan mode, a six-point R^2 calibration curve was prepared from 2 to 100 ppt for all other target compounds. Two compounds used a quadratic regression: 1,1,2,2-tetrachloroethane and 1,2,4,5-tetrachlorobenzene. The relative response factor (RRF) was calculated for each compound using one of the four Agilent internal standards (part number STM-341N-1): pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene. Agilent surrogate standards (part number STM-530-1) consisted of dibromofluoromethane, 1,2-dichloroethane-d_4, toluene-d_8, and 4-bromofluorobenzene. The internal and surrogate standards were prepared in methanol from the Agilent standards at a concentration of five parts per million (ppm), after which 1 µL was then purged with each 25 mL sample for a resulting concentration of 200 ppt.

Seven 1 ppt standards were prepared to calculate the MDL, accuracy, and precision calculations for 1,2-dibromoethane and 1,2,3-trichloropropane, and seven 10 ppt standards were prepared for all other target compounds. Ten 20 ppt standards were prepared for a midpoint calibration check, for accuracy and precision for all target compounds. Twenty-two additional 1 ppt water standards were prepared for a low-point calibration check of accuracy and precision for 1,2-dibromoethane and 1,2,3-trichloropropane. All calibration, MDL, accuracy, and precision standards were analyzed with the Lumin and AQUATek LVA conditions listed in Table 1. GC/MS conditions are shown in Table 2. Consumables and part numbers used in this method are shown in Table 3.

Instrument conditions

Table 1. Teledyne Tekmar Lumin P&T/AQUATek LVA conditions.

Parameter	Value
Standby	
Valve Oven Temp	150 °C
Transfer Line Temp	150 °C
Sample Mount Temp	90 °C
Standby Flow	20 mL/min
Purge Ready Temp	35 °C
MCS Purge Temp	20 °C
Purge	
Purge Temp	20 °C
Purge Time	8.00 min
Purge Flow	55 mL/min
Dry Purge Temp	20 °C
Dry Purge Time	1.00 min
Dry Purge Flow	100 mL/min
Sample Heater Enable	Off
Trap	9
Chiller Tray	Off
Purge Gas	Nitrogen

Parameter	Value
Desorb	
Desorb Preheat Temp	245 °C
Desorb Temp	250 °C
Desorb Time	0.50 min
Drain Flow	300 mL/min
GC Start Signal	Begin desorb
Bake	
Bake Time	4.00 min
Bake Temp	260 °C
MCS Bake Temp	180 °C
Bake Flow	200 mL/min
AQUATek LVA	
Sample Loop Time	0.85 min
Sample Transfer Time	1.25 min
Rinse Loop Time	0.85 min
Sweep Needle Time	0.30 min
Presweep Time	0.35 min
Water Temp	90 °C
Bake Rinse Cycles	1
Bake Rinse Drain Time	0.60 min

Table 2. Agilent 7890B GC/5977A MS system conditions.

Agilent 7890B GC Conditions	
Column	Agilent DB-624 UI, 30 m × 0.25 mm, 1.4 µm Column flow: 1.2 mL/min
Oven Profile	35 °C, 2 min, 12 °C/min to 100 °C, 30 °C/min to 230 °C, 2 min hold, Run time: 13.75 min
Inlet	200 °C, 5:1 Split, septum purge flow 0.75 mL/min Carrier gas: helium
Agilent 5977A MS Conditions	
Temp	Transfer line: 250 °C Source: 230 °C Quad: 150 °C
SIM/Scan	Range: *m/z* 35 to *m/z* 350 Solvent delay: 0.50 min SIM/Scan 100 Dwell time
SIM Ions	107, 109, 75, 110
Current	Gain factor: 25.00, auto tune

Table 3. Agilent consumables and part numbers.

Consumable	Description	Part Number
Trap	Trap, proprietary (#9), 12 × 1/8 inch, U-shape	5188-8816
Column	J&W DB-624 Ultra Inert; 30 m, × 0.25 mm, 1.4 µm	122-1334UI
Inlet Liner	Straight, Splitless Inlet Liner, Ultra Inert, 1 mm id	5190-4047
Inlet Seal	Gold Plated Inlet Seal, Ultra Inert, 10/pk	5190-6145
Inlet Column Ferrule	85:15 Vespel/Graphite Short Ferrule, 0.4 mm id, 10/pk	5181-3323
MSD Column Ferrule	85:15 Vespel/Graphite Long Ferrule, 0.4 mm id, 10/pk	5062-3508
Chemical Standards	VOC liquids standard, EPA 524.2	DWM-524A-1
Chemical Standards	Internal standard, EPA 8260B	STM-341N-1
Chemical Standards	VOC gas standard, EPA 524.2	DWM-544-1
Chemical Standards	Surrogate standard, EPA 8260B	STM-530-1

Results and discussion

The linear correlation coefficient of the calibration curve (R^2), MDL, midpoint calibration check, accuracy, and precision data are shown in Table 4. Table 5 displays the accuracy and precision of n = 22, 1 ppt water standards of 1,2-dibromoethane and 1,2,3-trichloropropane.

Table 4. Italian Legislative Decree 152/2006 calibration, accuracy, and precision data.

Compound	Calibration				Accuracy and Precision (n = 7, 10 ppt)			Midpoint Calibration Check (n = 10, 20 ppt)	
	Retention Time	Primary Ion	R^2	Average RRF	MDL (ppt)	Precision	Accuracy	Precision	Accuracy
Chloromethane	2.06	50	1.00	0.243	1.0	3.3	102	5.5	99
Vinyl Chloride	2.10	62	0.999	0.141	2.2	6.7	104	7.1	96
1,1-Dichloroethene	3.42	61	1.00	0.278	3.6	10.9	104	9.0	99
trans-1,2-Dichloroethene	4.19	61	1.00	0.326	3.1	9.9	98	7.8	104
1,1-Dichloroethane	4.60	63	1.00	0.500	2.4	7.9	96	6.9	99
cis-1,2-Dichloroethene	5.17	61	1.00	0.429	1.2	4.0	95	3.4	96
Chloroform	5.48	83	1.00	0.823	3.2	10.4	99	7.5	96
Dibromofluoromethane (Surr)	5.63	111	8.45	0.572		3.8	107	3.0	100
Pentafluorobenzene (IS)	5.68	168							
1,2-Dichloroethane-d_4 (Surr)	5.97	65	5.67	0.265		2.4	106	2.0	99
1,2-Dichloroethane	6.04	62	1.00	0.331	1.6	5.1	101	3.2	96
Benzene	6.04	78	1.00	1.37	2.7	8.4	101	7.9	97
1,4-Difluorobenzene (IS)	6.42	114							
Trichloroethene	6.69	130	1.00	0.370	4.0	12.5	101	9.4	103
1,2-Dichloropropane	6.90	63	1.00	0.203	3.1	9.8	100	6.8	97
Bromodichloromethane	7.19	83	1.00	0.398	3.9	13.0	96	6.0	91
Toluene-d_8 (Surr)	7.91	98	2.46	1.28		1.0	98	1.8	100
Toluene	7.97	91	0.999	1.25	4.0	13.2	97	6.7	89
Tetrachloroethene	8.47	166	0.999	0.772	3.5	11.4	99	7.7	91
1,1,2-Trichloroethane	8.31	97	0.999	0.209	1.8	6.2	91	6.1	91
Dibromochloromethane	8.65	129	0.999	0.281	4.8	16.3	94	4.8	88
1,2-Dibromoethane[2]	8.80	107	0.999	0.013	0.1	3.9	111	4.8	103
Chlorobenzene-d_5 (IS)	9.11	117							
Chlorobenzene	9.14	112	1.00	0.737	2.8	10.2	87	6.8	90
Ethylbenzene	9.22	91	0.998	0.933	3.3	11.0	96	7.8	93
m-, p-Xylene	9.30	91	0.997	0.777	3.9	7.1	88	8.5	84
o-Xylene	9.59	91	0.996	0.830	3.1	11.2	89	6.9	86
Styrene	9.59	104	0.997	0.841	2.7	9.4	90	8.2	86
Bromoform	9.72	173	0.999	0.157	4.6	18.0	82	8.7	87
4-Bromofluorobenzene (Surr)	9.95	95	4.93	0.468	2.2	2.2	102	2.9	102
1,1,2,2-Tetrachloroethane[1]	10.02	83	0.999	0.165	3.9	12.7	97	8.9	93
1,2,3-Trichloropropane[2]	10.22	75	0.998	0.257	0.1	2.6	100	5.7	91
1,4-Dichlorobenzene-d_4 (IS)	10.70	150							
1,4-Dichlorobenzene	10.71	146	1.00	0.833	3.4	12.1	89	5.0	93
1,2-Dichlorobenzene	10.94	146	0.999	0.716	2.9	10.4	89	7.6	95
1,2,4-Trichlorobenzene	11.87	180	0.996	0.432	2.1	7.5	90	11.8	110
Hexachlorobutadiene	11.97	225	0.996	0.466	2.0	7.5	84	6.3	85
1,2,4,5-Tetrachlorobenzene[1]	12.88	216	0.998	0.056	4.7	12.1	125	18.8	108

[1] Compound used a quadratic regression.
[2] MDL data from seven 1 ppt samples.

Table 5. 1,2-Dibromoethane and 1,2,3-trichloropropane accuracy and precision data.

Compound	Low-point Calibration Check (n = 22, 1 ppt)		
	Average (ppt)	Precision	Accuracy
1,2-Dibromoethane	1.08	7.4	108
1,2,3-Trichloropropane	1.05	7.5	105

Conclusion

This application note demonstrates the capability of the Teledyne Tekmar Lumin P&T paired with an AQUATek LVA and an Agilent 7890B GC and Agilent 5977A MS to demonstrate compliance with Italian Legislative Decree 152/2006. Using SIM mode, the required 0.1 ppt detection limit was achieved for 1,2-dibromoethane and 1,2,3-trichloropropane in water samples. In full scan mode, the rest of the target compounds passed all method requirements: $R^2 \geq 0.995$, MDL ≤ 5 ppt, midpoint calibration check precision ≤ 20%, and accuracy ± 20% with an average recovery of 95%.

The results of the low-point calibration check study demonstrate that this system performs automated determination of 1,2-dibromoethane and 1,2,3-trichloropropane at the sensitivity required by Italian Legislative Decree 152/2006.

Reference

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

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