

Italian Legislative Decree 152/2006 Using the Tekmar Atomx XYZ 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 Atomx XYZ purge and trap (P&T) VOC sample preparation system combined with 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 regression (r^2) calibration curve and method detection limits (MDLs) for target compounds.

Introduction

Article 275 of Italian Legislative Decree 152/2006, Annex III Part 5 describes the regulation of VOCs in water, as well as method parameter limitations and guidelines. As stated within these VOC regulations, the two compounds, 1,2-Dibromoethane and 1,2,3-Trichloropropane, have legal limits at the low level of 1 ppt in water. Traditionally, a method requiring this level of sensitivity uses a 25 mL sample sparge. This application note will demonstrate achieving the required sensitivity with a 5 mL sample sparge.

The Atomx XYZ is Teledyne Tekmar's most advanced P&T system and is based on the time-tested Atomx instrument platform. The concentrator's efficient trap cooling design reduces sample cycle time by as much as 14% over the previous model. Combined with its 84-position soil and water autosampler, the result is more samples tested per 12-hour period. 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 Atomx XYZ incorporates a precision-machined valve manifold block to reduce potential leak sources and ensure the system is both reliable and robust.

Sample Preparation

Working calibration standards for each calibration point were prepared in 1 mL of methanol from a 25 ppb calibration standard made from the two following Restek® standards: 1,2-Dibromoethane and 1,2,3-Trichloropropane. Methanol compensation was used in each calibration point to prevent any interferences related to methanol volume variance.

An eight-point linear regression (r^2) calibration curve was prepared from 0.1 ppt to 50 ppt for both compounds with $r^2 \geq 0.995$. The relative response factor (RF) was calculated for each compound using one internal standard: Fluorobenzene. The internal standard was prepared in methanol from the Restek standard at a concentration of 25 ppb, after which 5 μ L was then mixed with each 5 mL sample for a resulting concentration of 25 ppt.

Seven 0.5 ppt standards were prepared to calculate the method detection limit (MDL), accuracy and precision calculations. All calibration, MDL, accuracy and precision standards were analyzed with the Atomx XYZ conditions in [Table I](#). GC-MS conditions are shown in [Table II](#).

Experimental Instrument Conditions

Table I Teledyne Tekmar Atomx XYZ Water Method Conditions			
Standby	Variable	Desorb	Variable
Valve Oven Temp	140 °C	Water Needle Rinse Volume	7.00 mL
Transfer Line Temp	140 °C	Sweep Needle Time	0.25 min
Sample Mount Temp	90 °C	Desorb Preheat Temp	245 °C
Water Heater Temp	90 °C	Desorb Time	2.00 min
Sample Vial Temp	20 °C	Drain Flow	300 mL/min
Soil Valve Temp	100 °C	Desorb Temp	250 °C
Standby Flow	10 mL/min	Methanol Needle Rinse	Off
Purge Ready Temp	40 °C	GC Start Signal	Begin Desorb
Purge	Variable	Bake	Variable
Sample Equilibrate Time	0.00 min	Methanol Glass Rinse	Off
Pre-sweep Time	0.25 min	Water Bake Rinses	1
Prime Sample Fill Volume	3.00 mL	Water Bake Rinse Volume	7.00 mL
Sample Volume	5.00 mL	Bake Rinse Sweep Time	0.25 min
Sweep Sample Time	0.25 min	Bake Rinse Sweep Flow	100 mL/min
Sweep Sample Flow	100 mL/min	Bake Rinse Drain Time	0.40 min
Spurge Vessel Heater	Off	Bake Time	20.0 min
Purge Time	11.00 min	Bake Flow	200 mL/min
Purge Flow	40 mL/min	Bake Temp	280 °C
Purge Temp	20 °C	Condensate Bake Temp	180 °C
Condensate Purge Temp	20 °C		
Dry Purge Time	2.00 min	Trap	9
Dry Purge Flow	100 mL/min	Chiller Tray	Off
Dry Purge Temp	20 °C	Purge Gas	Nitrogen

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 °C, 2 min, 12 °C/min to 85 °C, 20 °C/min to 225 °C, 2 min Hold, Run Time 15.167 min
Inlet	200 °C, 60:1 Split
Thermo Scientific ISQ 7000 MS Conditions	
Temp	Transfer Line 230 °C; Ion Source 300 °C
Sim Ions	Fluorobenzene: 96, 1,2-Dibromoethane: 107, 109, 1,2,3-Trichloropropane: 75, 79, 110, Solvent Delay 0.10 min, Dwell/Scan Time Fluorobenzene: 0.1 sec, 1,2-Dibromoethane: 0.05, 0.05 sec, 1,2,3-Trichloropropane: 0.05, 0.05, 0.05 sec.
Current	Chrom. Filter Peak Width (sec) Fluorobenzene and 1,2-Dibromoethane: 1.000, 1,2,3-Trichloropropane: 1.500, Emission Current 50 µA, Gain 5.00E+006

Results

The linear correlation coefficient of the calibration curve (r^2), MDL, accuracy and precision data are shown in Table III. Figure 1 displays a 20 ppt 1,2-Dibromoethane standard, indicating excellent peak resolution with minimal water interference. Figure 2 displays a 20 ppt 1,2,3-Trichloropropane standard, indicating excellent peak resolution with minimal water interference.

Table III Italian Legislative Decree 152/2006 Calibration, Accuracy and Precision Data							
Compound	Calibration				Accuracy and Precision (n=7, 0.5 ppt) ¹		
	Retention Time	Linearity ($r^2 \geq 0.995$)	Avg. RF	MDL (ppt) ¹	Avg. Conc. (ppt)	Accuracy (%)	Precision ($\leq 20\%$)
Fluorobenzene (IS)	4.97						
1,2-Dibromoethane	7.22	0.997	0.406	0.05	0.45	90	3.64
1,2,3-Trichloropropane	8.92	0.995	0.605	0.07	0.44	89	5.27

1. Data from seven 0.5 ppt samples.

Figure 1 MS Quantitation of a 20 ppt 1,2-Dibromoethane Standard Indicating Excellent Peak Resolution with Minimal Water Interference and a $r^2 = 0.997$.

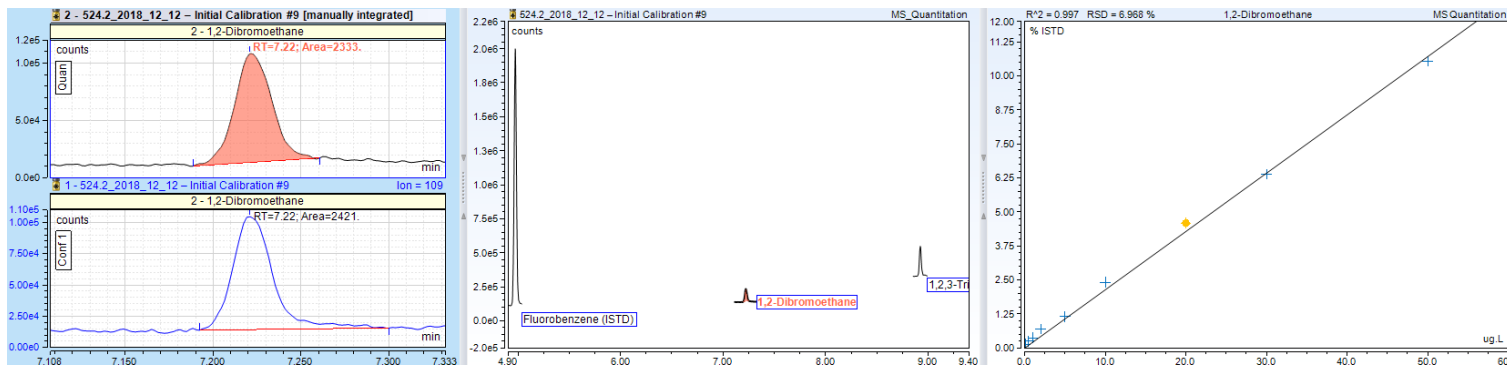
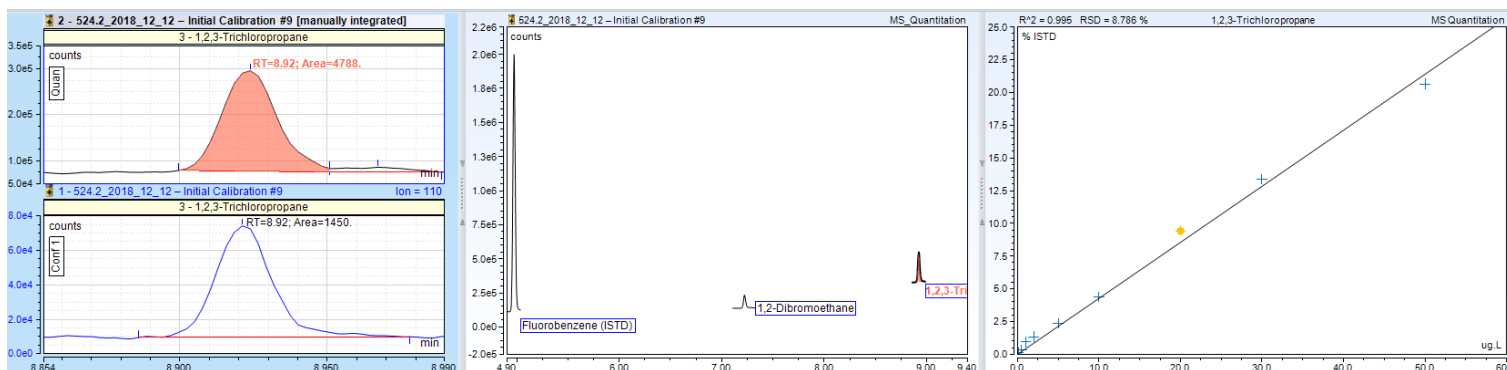


Figure 2 MS Quantitation of a 20 ppt 1,2,3-Trichloropropane Standard Indicating Excellent Peak Resolution with Minimal Water Interference and a $r^2 = 0.995$.



Conclusion

This study demonstrates the capability of the Teledyne Tekmar Atomx XYZ purge and trap (P&T) VOC sample preparation system to process 1,2-Dibromoethane and 1,2,3-Trichloropropane in water samples following Article 275 of Italian Legislative Decree 152/2006, Annex III Part 5, with detection by a Thermo Scientific TRACE 1310 GC/ISQ 7000 MS with an AEI source. With only a 5 mL sample sparge, the linearity of the calibration curve from 0.1 ppt to 50 ppt passed all method requirements with minimal interference from excessive water. The MDL and accuracy and precision for seven 0.5 ppt standards also indicated minimal interference from excessive water.

References

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