

Analysis of Epichlorohydrin in Drinking Water Using the Tekmar Atomx XYZ P&T and the Agilent 8890 GC and 5977C MS

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water testing, GC/MS, Agilent GC/MS, Tekmar Atomx XYZ Purge and Trap, Epichlorohydrin

Abstract

Epichlorohydrin (ECH) is a versatile starting material in the production of drugs and polymers and is also used as an insect fumigant and solvent for organic synthesis reactions. ECH-based polymer pipes are widely employed in the production of drinking water. Due to its extreme reactivity and toxicity, many nations have begun imposing limits on the amount of ECH allowable in drinking water, including the new European Union Directive 2020/2184 requiring a limit of 100 parts per trillion (ppt). Many European countries go beyond this, recommending compliance at 1/3 this limit, indicating a 30 ppt minimum detection limit (MDL).

In the United States, drinking water analysis of Volatile Organic Compounds (VOCs) is performed by Purge and Trap (P&T) concentration, using standard United States Environmental Protection Agency (EPA) methods. In Europe, most drinking water detection limits are achieved with static headspace, but in order to reach the desired 30 ppt MDL, P&T will be used in this application. Variations EPA drinking water methods, with modifications to the matrix and method parameters, will be made to prepare the drinking water samples by the Teledyne LABS Tekmar Atomx XYZ P&T concentrator with analysis performed by an Agilent 8890 Gas Chromatograph (GC) and 5977C Mass Spectrometer (MS) (GC/MS). Calibration data, MDL, mid-point calibration check, and accuracy and precision of n=40, 30 ppt ECH samples will also be presented.

Introduction

The Tekmar Atomx XYZ is Teledyne LABS' 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, 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

Two working calibration standards were prepared in methanol at the concentrations of 100 parts per billion (ppb) and 500 ppb from a commercially available ECH standard.

An eight-point linear correlation coefficient (r^2) calibration curve was prepared from 10 to 500 ppt with regression value (r^2) ≥ 0.995 . The relative response factor (RRF) was calculated for ECH using the internal standard: 1,4-difluorobenzene. The internal standard was prepared in methanol from a commercially available 1,4-difluorobenzene standard at a concentration of 200 parts per billion (ppb), after which 5 μ L was then mixed with each 5 mL sample for a resulting concentration of 200 ppt.

Seven 30 ppt standards were prepared to calculate the MDL. Also, seven 100 ppt 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 Atomx XYZ conditions in Table I. GC-MS conditions are shown in Table II.



Experimental Instrument Conditions

Table I Tekmar Atomx XYZ P&T Water Method Conditions			
Standby	Variable	Desorb	Variable
Valve Oven Temp	140 °C	Methanol Needle Rinse	Off
Transfer Line Temp	140 °C	Water Needle Rinse Volume	7.00 mL
Sample Mount Temp	90 °C	Sweep Needle Time	0.25 min
Water Heater Temp	90 °C	Desorb Preheat Temp	245 °C
Sample Cup Temp	20 °C	GC Start Signal	Begin Desorb
Soil Valve Temp	50 °C	Desorb Time	1.00 min
Standby Flow	10 mL/min	Drain Flow	300 mL/min
Purge Ready Temp	40 °C	Desorb Temp	250 °C
Purge	Variable	Bake	Variable
Sample Equilibrate Time	0.00 min	Methanol Glass Rinse	Off
Pre-sweep Time	0.25 min	Water Bake Rinses	2
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	2.00 min
Purge Time	11.00 min	Bake Flow	200 mL/min
Purge Flow	40 mL/min	Bake Temp	260 °C
Purge Temp	20 °C	MCS Bake Temp	200 °C
MCS Purge Temp	20 °C		
Dry Purge Time	0.50 min	Trap	Vocarb 3000 (K)
Dry Purge Flow	100 mL/min	Chiller Tray	On, 10 °C
Dry Purge Temp	20 °C	Purge Gas	Nitrogen

Table II Agilent 8890 GC and 5977C MS System Conditions	
Agilent 8890 GC Conditions	
Column	DB-624 UI, 20 m x 0.18 mm, 1µm Film, Column Flow – 0.8 mL/min
Oven Profile	40 °C, 1 min, 12 °C/min to 130 °C, 40 °C/min to 220 °C, 1 min, Run Time 11.75 min
Inlet	200 °C, 30:1 Split, Septum Purge Flow 0.5 mL/min, 16.53 psi, Carrier Gas - Helium
Agilent 5977C MS Conditions	
Temp	Transfer Line 250 °C; Source 230 °C; Quad 150 °C
SIM	1,4-Difluorobenzene ions – 114; Epichlorohydrin ions – 57,49,62; Solvent Delay 3.50 min, Dwell Time 100
Current	Gain Factor 15, BFB Auto Tune

Results

The linear correlation coefficient of the calibration curve (r^2), MDL, and mid-point calibration check standard data are shown in Table III. Figure 1 displays the linear correlation coefficient calibration curve for ECH. In addition, a long-term, 40 sample, 30 ppt low-point calibration check standard study was performed with the data shown in Table IV. Figure 2 displays a 30 ppt ECH standard in water in SIM mode with confirmation ion 57 m/z and two secondary ions 62 and 49 m/z. Figure 3 displays a 100 ppt ECH standard in water in SIM mode with confirmation ion 57 m/z and two secondary ions 62 and 49 m/z. Figure 4 displays the results of the ECH long-term calibration check standard study.

Table III Epichlorohydrin Calibration, MDL, and Mid-Point Calibration Check Standard Data									
Compound	Calibration (10-500 ppt)				Method Detection Limits (n=7, 30 ppt)			Mid-Point Calibration Check (n=7, 100 ppt)	
	Ret. Time	Confirm. Ion	Cal Type	Linearity ($r^2 \geq 0.995$)	MDL (ppt)	Precision ($\leq 20\%$)	Accuracy ($\pm 30\%$)	Precision ($\leq 20\%$)	Accuracy ($\pm 30\%$)
1,4-Difluorobenzene (IS)	4.44	114							
Epichlorohydrin	5.43	57	LIN	0.9997	4.4	4.7	99	3.0	93

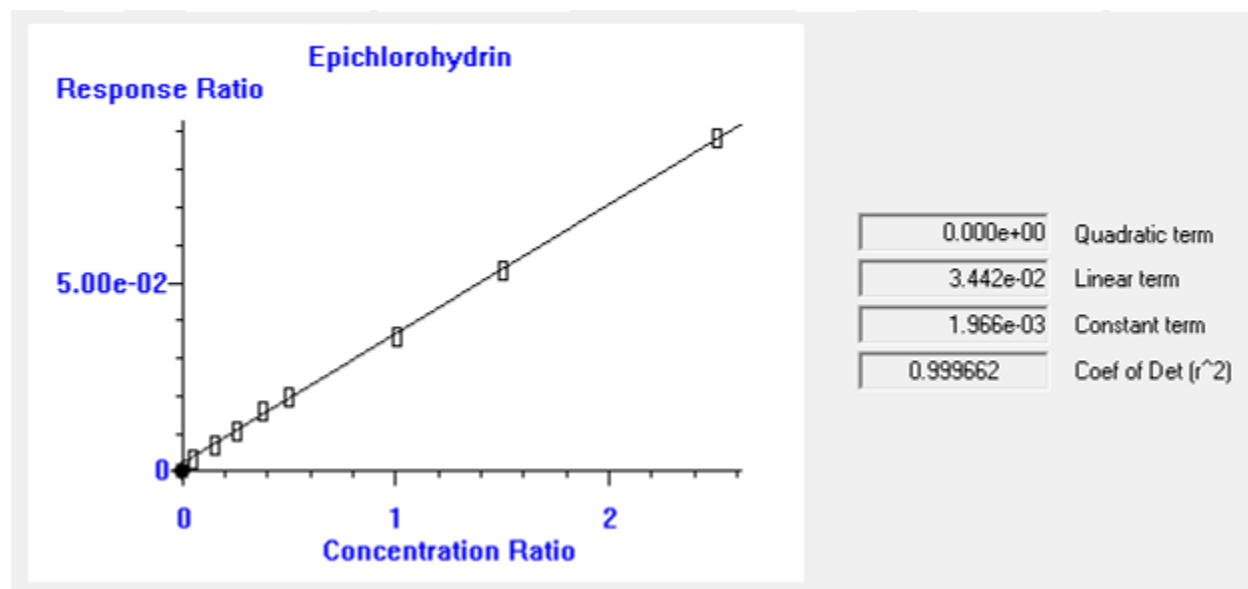


Figure 1 ECH linear correlation coefficient (r^2) calibration curve fit, 10-500 ppt.

Table IV Epichlorohydrin Long-Term Calibration Check Data		
Compound	Long-Term Calibration Check (n=40, 30 ppt)	
	Precision ($\leq 20\%$)	Accuracy ($\pm 20\%$)
Fluorobenzene (IS)		
Epichlorohydrin	4.3	92

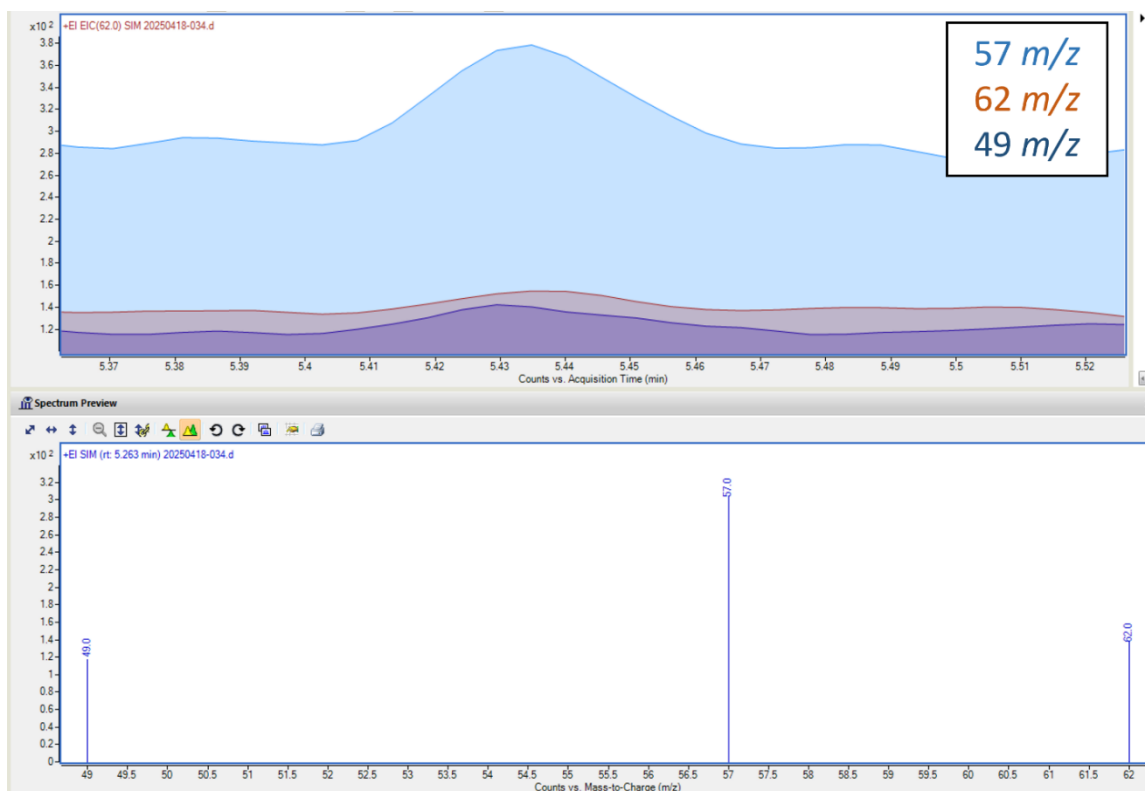


Figure 2 Total ion chromatogram (TIC) of 30 ppt ECH standard in a drinking water sample with confirming ion (57 m/z) and two secondary ions (62 and 49 m/z).

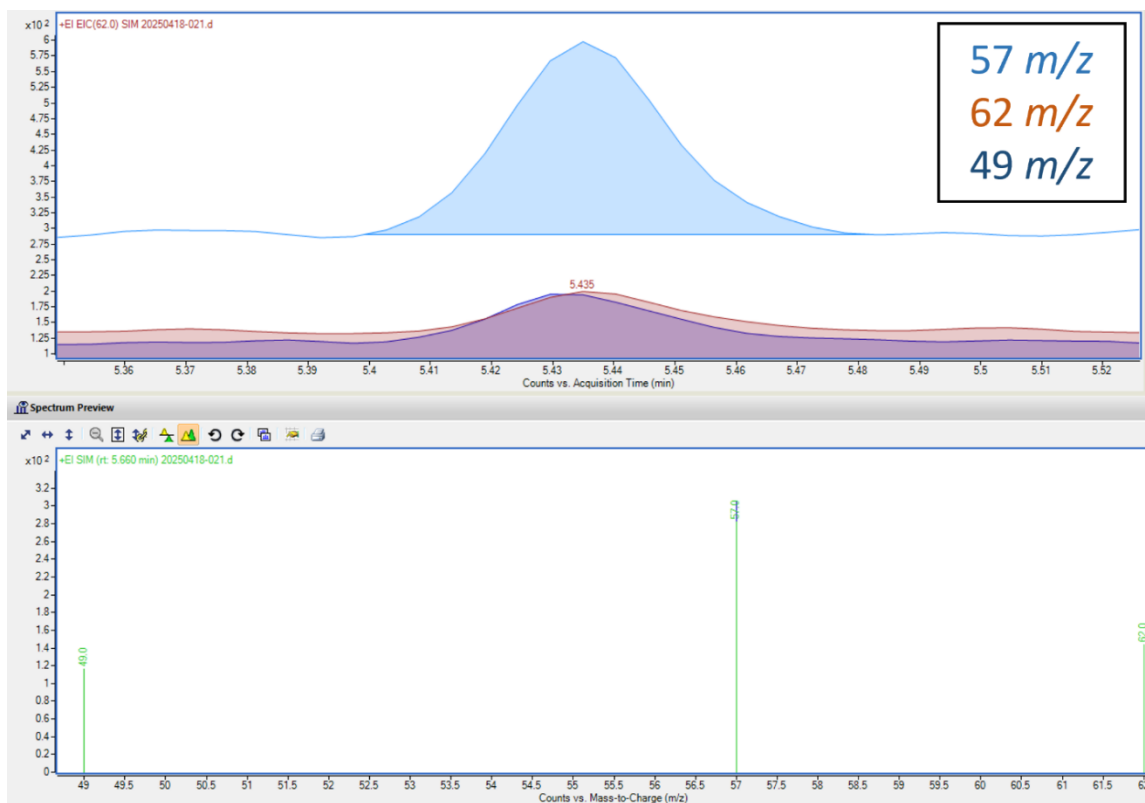


Figure 3 TIC of 100 ppt ECH standard in a drinking water sample with confirming ion (57 m/z) and two secondary ions (62 and 49 m/z).

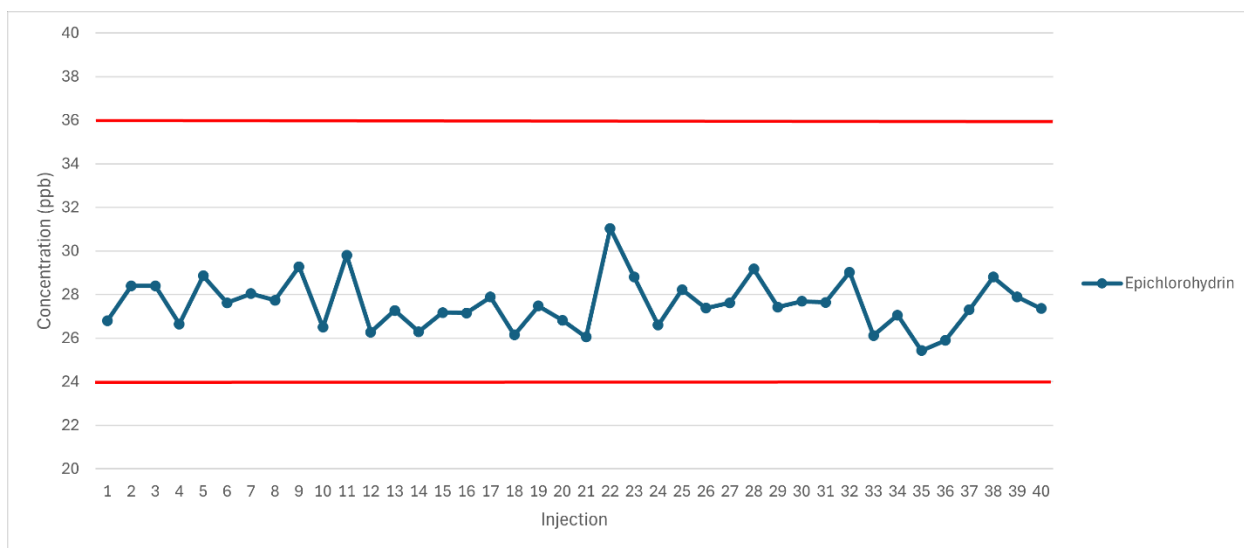


Figure 4 Results of long-term study, n=40, 30 ppt ECH standard in drinking water samples. Red lines represent $\pm 20\%$ accuracy method requirement for continuing calibration check standards.

Conclusion

This study demonstrates the capability of the Teledyne LABS Tekmar Atomx XYZ P&T concentrator to process low-level ECH in drinking water samples with detection by an Agilent 8890 GC and 5977C MS. The linearity of the calibration curve from 10 to 500 ppt passed method requirements, including the verification of the initial calibration curve with the 10 ppt passing the lower standard (LLOQ) recalculation within $\pm 50\%$ of its true value and the rest of the calibration curve ($> \text{LLOQ}$) passing with $\pm 30\%$ of their true value. The blank after the highest point of the calibration curve passed method carryover requirements by remaining $< 1/2$ the LLOQ. Furthermore, the application proved robust during a long-term study with 40 samples of a 30 ppt ECH standard with 4.3% precision and 92% accuracy of the recovery.

References

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