Analysis of Epichlorohydrin in Drinking Water Using the Lumin P & T Concentrator

Application Note

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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.

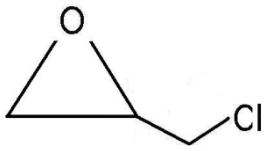
Drinking water analysis of Volatile Organic Compounds (VOCs) is normally performed by purge and trap concentration, using standard US EPA methods. Variations of these methods, with modifications to the matrix and method parameters, will be made to prepare the drinking water samples for analysis by Gas Chromatograph/Mass Spectrometer (GC/MS). Calibration data and method detection limits will also be presented.

Introduction

Epichlorohydrin (ECH), or 1-chloro-2,3-epoxypropane, is a versatile starting material in the production of drugs, epoxy coating materials, glycerol, and polymers with high wet strength for the paper industry. Other major applications of ECH include use as an insect fumigant, solvent for synthetic resins, and starting material for the production of paints and varnishes. Also, ECH-based polymer pipes are widely employed in the production of drinking water as well as syntheses of cationic polyelectrolytes, which are used in surface water and wastewater clarification.[1]

Due to the presence of chlorine and an epoxy bridge, ECH (Figure 1) is a highly reactive molecule. ECH tends to hydrolyze in water at ambient temperature to form 3-MCPD (3-monochloropropane-1,2-diol or 3-chloro-1,2-propanediol), a carcinogen. The hydrolysis of ECH is accelerated in the presence of heat and acid.[2]

Figure 1 Epichlorohydrin Structure.



ECH is toxic by inhalation and dermal/oral adsorption and can be dangerous to the human central nervous system. ECH is also a potential mutagen that reacts with human cellular components.[3-5] The International Agency of Research on Cancer (IARC) has classified ECH as a group 2A, probable carcinogen.[6]

The European Normative 98/83/EC on the quality of waters intended for human consumption has imposed a quality limit of 0.1 µg/L (ppb) ECH for water made drinkable by treatment.[7] This application note will utilize the Teledyne Tekmar Lumin Purge and Trap Concentrator (PTC) and AQUATek100 autosampler for complete automation of P & T concentration and analysis of drinking water samples.

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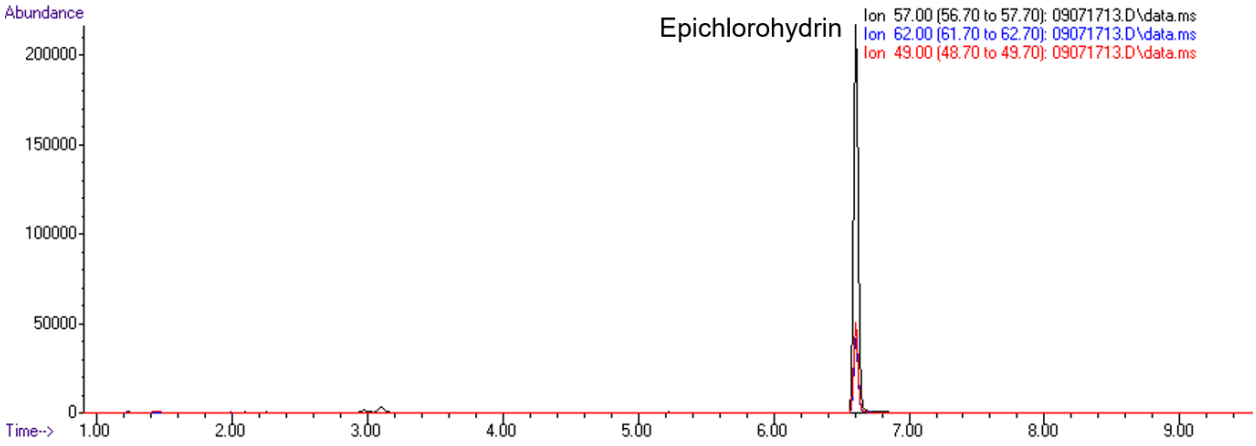
A 5 mL sample volume was utilized for this analysis. ECH was purged from the sample and on to a sorbent trap (Tenax Stamp 1A). The trap was then heated and the analyte was desorbed to the GC/MS. Using the Agilent 7890B/5977A GC/MS in Selective Ion Monitoring (SIM) mode, an average response factor calibration was performed. Percent Relative Standard Deviation (%RSD) and Method Detection Limits (MDL) were also determined. An example of a SIM scan for ECH is shown in Figure 2.

Figure 2 Selective Ion Monitoring (SIM) Scan of 50.0 ppb Epichlorohydrin Standard (RT 6.61 Min).



Sample Preparation

A 50 ppm ECH stock standard was prepared in methanol. Calibration standards were prepared in a volumetric flask filled with 10% (w/v) sodium chloride de-ionized water over a range of 0.1 ppb to 50 ppb. All samples were prepared and transferred to headspace free 40 mL VOA vials for analysis. All calculations were performed using the Agilent Environmental ChemStation™ software to process the calibration and sample data.

Experimental-Instrument Conditions

The Lumin and AQUATek 100 autosampler were coupled to an Agilent 7890B/5977A GC/MS for analysis. A Tenax® Stamp 1A trap was the analytical trap of choice. The GC was configured with a Restek® VMS 20 m x 0.18 mm x 1.0 µm column. Lumin and AQUATek 100 instrument parameters are shown in Table I. GC/MS parameters are shown in Table II.

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Table I Lumin and AQUATek 100 Conditions			
Standby	**Variable**	**Bake**	**Variable**
Valve Oven Temp	140 °C	Bake Time	2.00 min
Transfer Line Temp	140 °C	Bake Temp	230 °C
Sample Mount Temp	90 °C	MCS Bake Temp	200 °C
Purge Ready Temp	35 °C	Bake Flow	250 mL/min
MCS Purge Temp	20 °C	**AQUATek 100**	**Variable**
Standby Flow	10 mL/min	Sample Loop Time	0.50 min
Purge	**Variable**	Sample Transfer Time	1.25 min
Purge Time	11.00 min	Rinse Loop Time	0.85 min
Purge Flow	200 mL/min	Sweep Needle Time	0.30 min
Dry Purge Temp	20 °C	Presweep Time	0.35 min
Dry Purge Time	0 min	Water Temp	90 °C
Dry Purge Flow	0 mL/min	Bake Rinse Drain Cycles	3
Desorb	**Variable**	Bake Rinse Drain Time	0.60 min
Desorb Preheat Temp	175 °C		
Desorb Time	2.00 min	**Trap**	Tenax Stamp 1A
Desorb Temp	185 °C	**Chiller Tray**	On, 10 °C
Drain Flow	300 mL/min	**Purge Gas**	Helium

Table II Agilent 7890B GC and 5977A MSD System Conditions	
Agilent 7890B GC Conditions	
Column	Restek® VMS 20 m x 0.18 mm x 1.0 µm
Oven Profile	35 °C for 3 min, to 100 °C at 15 °C/min, for 0 min, to 240 °C at 25 °C/min for 2 min
Inlet	220 °C; 50:1 Split
Agilent 5977A MSD Conditions	
Temp	Transfer Line 230 °C; Source 230 °C; Quad 150 °C
Sim Ions	57,49,62
Dwell Time	100 msec per ion

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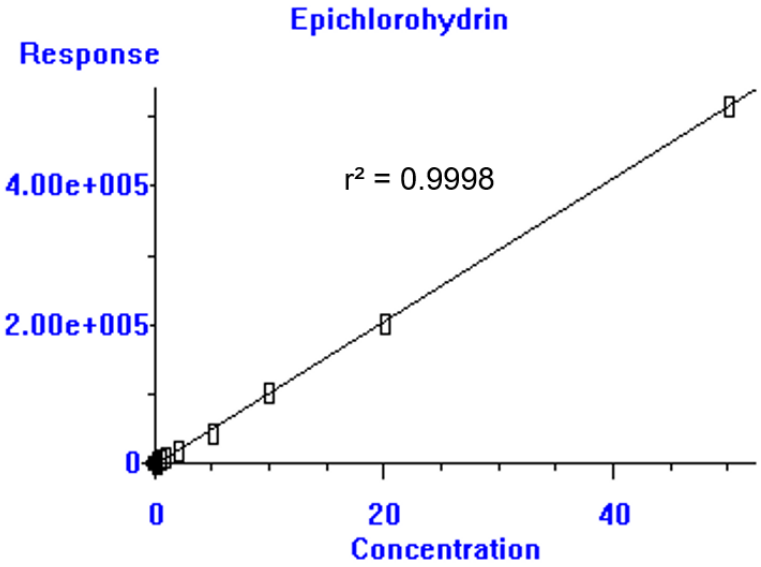
Calibration/ Results

The linear calibration curve for ECH is shown in Figure 3. ECH displayed a 0.9998 coefficient of determination (r^2) over the range of 0.1 ppb to 50 ppb.

Figure 3 Calibration Curve (0.1 to 50 ppb) for Epichlorohydrin.



The lowest point of calibration required by the regulatory body is 0.1 ppb. To verify that this level is both precise and accurate, a reproducibility test was performed. Seven duplicate samples were prepared at 0.1 ppb. An example of a SIM scan for ECH at 0.1 ppb is shown in Figure 4. These seven duplicate samples were analyzed to establish a Minimum Detection Limit (MDL) for ECH. The reproducibility and MDL results can be found in Table III.

Figure 4 Selective Ion Monitoring (SIM) Scan of 0.1 ppb Epichlorohydrin Standard (RT 6.61 Min).

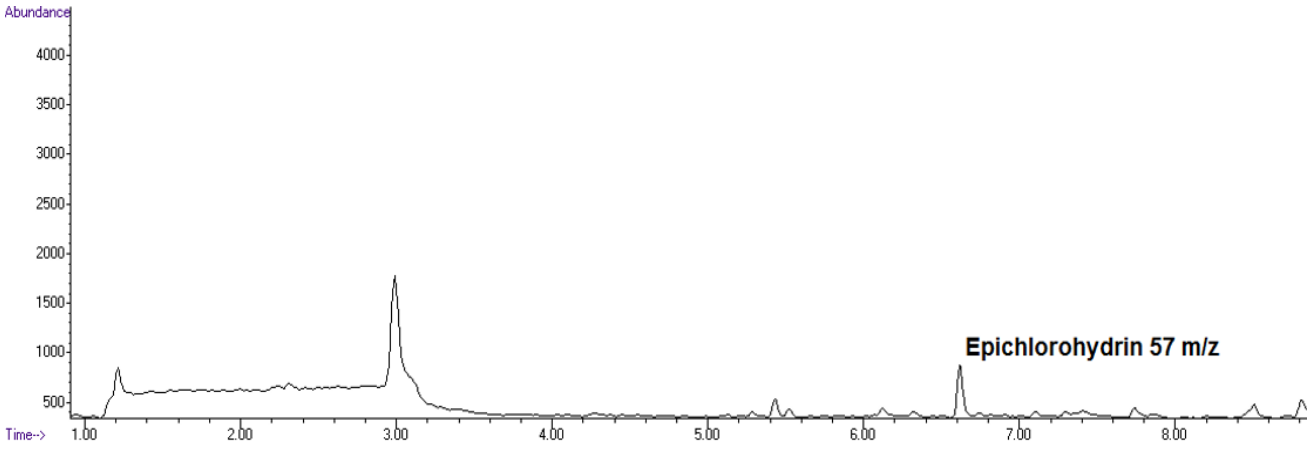


Table III Reproducibility and MDL for Epichlorohydrin[1]	
Sample Rep	**Concentration (ppb)**
1	0.11
2	0.10
3	0.10
4	0.10
5	0.09
6	0.09
7	0.09
Average	**0.097**
%RSD	**8.25%**
MDL	**0.024**

1 - All samples were within +/-20% of the original value.

To demonstrate the robustness of this method, twenty 1.0 ppb check standards were analyzed five days after the initial calibration curve was performed. The average response from these check standards resulted in a 98% recovery from the original calibration response value.

Conclusions

When conducting drinking water analysis, it is imperative to achieve high levels of accuracy and precision to protect public health and safety. Detecting chemical impurities, such as ECH, is critical to water suppliers due to stringent regulations enforced by their governing body. The European Normative 98/83/EC recommends limiting the concentration of ECH to 0.1 ppb in water for human consumption. By using the Lumin PTC and AQUATek 100 autosampler with an Agilent 7890B/5977A GC/MS with SIM scan, ECH was detected down to 0.1 ppb level (Figure 3). The results of this study demonstrate that the Lumin PTC with AQUATek100 easily performs automated determination of ECH and provide the sensitivity required by European Normative 98/83/EC.

References

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