Analysis of Epichlorohydrin in Drinking Water by Purge and Trap GC/MS

Abstract

Epichlorohydrin (ECH) is a versatile starting material in the production of drugs and polymers. It is also used as an insect fumigant and a 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 foreign 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 on these methods with modifications to the matrix and method parameters will be made to prepare the drinking water samples for analysis by GC/MS. Calibration data and method detection limits will also be presented.

Introduction

Epichlorohydrin (ECH), or 1-chloro-2, 3-epoxypropane is a common precursor used in the production of drugs, epoxy coating materials, glycerol, and polymers with high wet strength for paper industry. Other major applications include use as an insect fumigant, solvent for synthetic resins, and starting material for the production of paints and varnishes.[1] 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 epichlorohydrin (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]

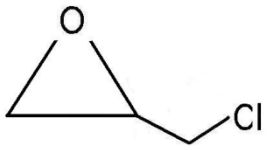

Figure 1: Epichlorohydrin structure

ECH, toxic by inhalation, dermal and oral adsorption, 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) for “water made drinkable by treatment”.[7] The work presented in this application note will utilize the Teledyne Tekmar Stratum Purge and Trap Concentrator (PTC) and AQUATek100 autosampler. This set-up allows for complete automation of sample preparation for the analysis of liquid water samples. A 25mL sample size will be employed for this analysis. In purge and trap concentration, analytes such as ECH are purged from the water sample onto a sorbent trap, in this case the Vocarb 3000. The trap is heated and analytes are desorbed to the GC/MS. Using the Agilent 7890/5975 GC/MS in Selective Ion Monitoring (SIM) mode, a linear calibration was preformed and percent Relative Standard Deviation (%RSD), Method Detection Limits (MDL) were also determined. An example of a SIM scan for ECH can be found in Figure 2.

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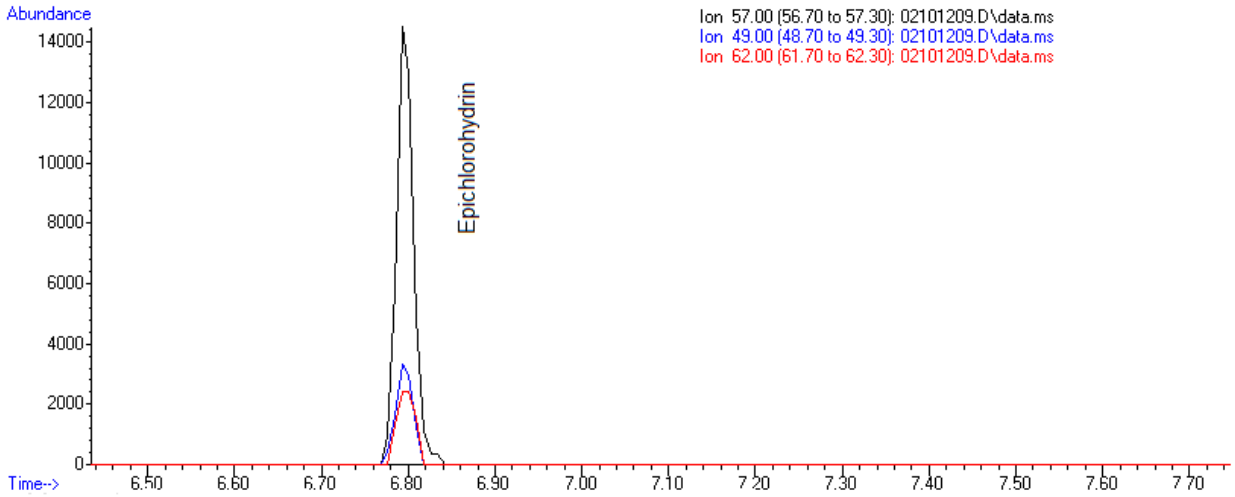

Figure 2: Selective Ion Monitoring (SIM) scan (m/z 57, 49 and 62) of 10.0 ppb Epichlorohydrin standard (RT 6.85min)

Experimental-Instrument Conditions

The Stratum PTC and AQUATek 100 autosampler equipped with a chiller were coupled to an Agilent 7890/5975 Gas Chromatograph Mass Spectrometer (GC/MS) for analysis. A Vocarb 3000 (K trap) was the analytical trap of choice. The GC was configured with a Restek Rtx-624 20m x 0.18mm x 1.0µm column. The GC/MS parameters are outlined in Table 1 and 2. Table 3 outlines the PTC and autosampler conditions.

GC Parameters	
GC:	Agilent 7890A
Column:	Restek Rtx-624 20m x 0.18mm x 1.0µm
Oven Program:	35° C for 3 min, to 100° C at 15° C/min, for 0 min, to 240° C at 25° C/min
Inlet:	220° C
Column Flow:	1.0 mL/min
Gas:	Helium
Pressure:	19.752 psi
Split Ratio:	50:1

MS Parameters	
MSD:	Agilent 5975 TAD
Source:	250° C
Quad:	200°C
Solvent Delay:	0.5 min
SIM Ions:	57,49,62
Dwell Time:	100 msec per ion
MS Transfer Line Temp:	230°

Tables 1 & 2: GC and MSD Parameters

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Stratum PTC and AQUATek 100 Parameters			
Variable	Value	Variable	Value
Pressurize Time	0.85 min	Purge Time	11.00 min
Sample Transfer Time	1.25 min	Purge Temp	20°C
Rinse Loop Time	0.85 min	Purge Flow	200 mL/min
Sweep Needle Time	0.30 min	Dry Purge Time	1.00min
Bake Rinse	On	Dry Purge Temp	20°C
Bake Rinse Cycles	3	Dry Purge Flow	100 mL/min
Bake Rinse Drain Time	0.60 min	GC Start	Start of Desorb
Presweep Time	0.35 min	Desorb Preheat Temp	175°C
Water Temp	90° C	Desorb Time	2.00 min
Valve Oven Temp	140°C	Desorb Temp	185°C
Transfer Line Temp	140°C	Drain Flow	300 mL/min
Sample Mount Temp	90°C	Bake Time	2.00 min
Purge ready Temp	35°C	Bake Temp	280°C
Condenser Ready Temp	40°C	Bake Flow	250 mL/min
Condenser Purge Temp	20°C	Condenser Bake Temp	200°C
Standby Flow	10 mL/min		
Pre-Purge Time	0.50min		
Pre-Purge Flow	40 mL/min		
Sample Heater	Off		
Sample Preheat Time	0.01 min		
Sample Temp	40°C		

Table 3: Stratum PTC and AQUATek 100 Parameters (Stratum PTC Parameters are in Blue, Parameters in Yellow were not used)

Calibration/ Results

A 10.0ppb ECH stock standard was prepared in methanol. Calibration standards were prepared in volumetric flask filled with 10% (w/v) sodium chloride de-ionized water over a range of 0.1ppb to 50ppb. All samples were prepared cold and transferred to headspace free 40mL VOA vials for analysis. All calculations were performed by using Agilent Chemstation software to process the calibration and sample data.

Relative response factors (RRF) for ECH were evaluated for %RSD and coefficient of determination (r^2) with the results listed in Table 4. The calibration curve for ECH can be seen in Figure 3.

Compound Name	Average RRF	%RSD	r^2
Epichlorohydrin (ECH)	2.116	3.75	0.9995

Table 4: Calibration data, for Epichlorohydrin

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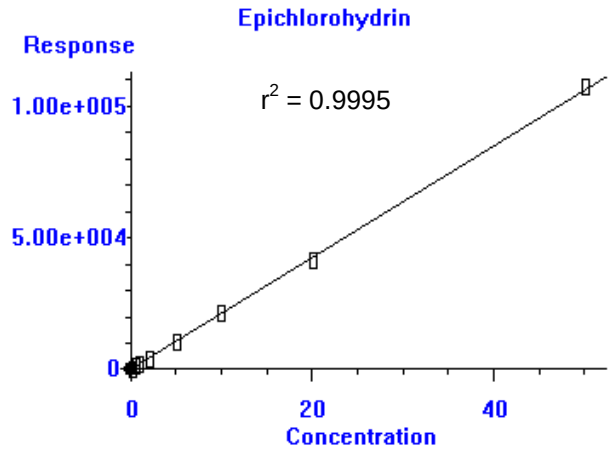

Figure 3: Calibration Curve (0.1 to 100 ppb) for Epichlorohydrin

The low point of calibration required by the regulatory body is 0.1ppb. To verify that this level can be detected precisely and accurately, a reproducibility test was performed. Seven reokucate samples were prepared at 0.1ppb. An example of a SIM scan for ECH at 0.1ppb can be found in Figure 4. These seven duplicate samples were analyzed to establish an MDL for ECH. The reproducibility and MDL results can be found in Table 5.

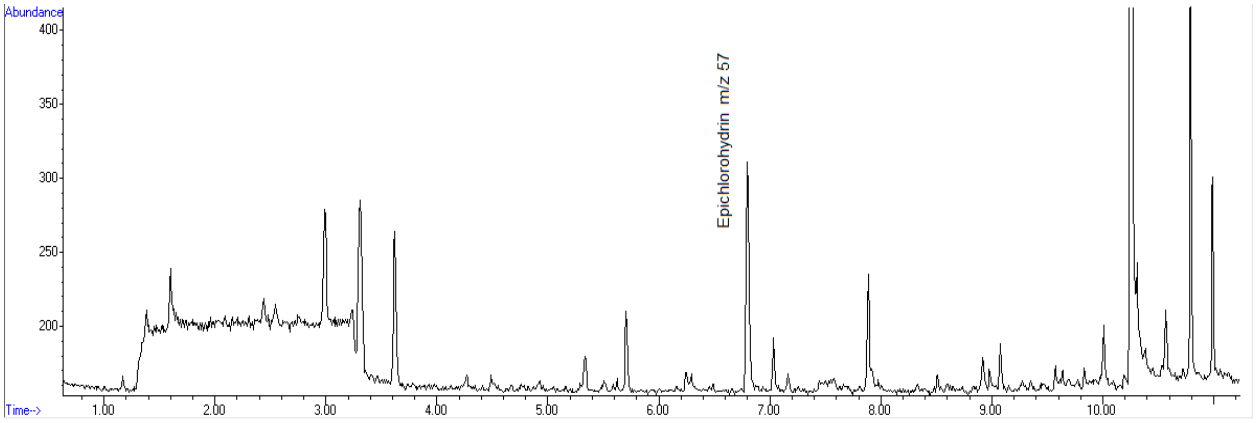

Figure 4: selective Ion Monitoring (SIM) scan of 0.1 ppb Epichlorohydrin standard (RT 6.85min)

Sample Rep	Area	Concentration (ppb)
1	198	0.09
2	174	0.08
3	187	0.09
4	185	0.09
5	171	0.08
6	166	0.08
7	164	0.08
Avg		0.084
%RSD		6.34%
MDL		0.016

Table 5: Reproducibility and MDL for Epichlorohydrin
*All sample were within +/-20% of the original valve

To demonstrate the robustness of this method a 1.0ppb check standard was analyzed three and four days after the initial calibration curve was performed. This data can be found in Table 6.

Compound Name	Response	Concentration (ppb)	% Recovery	Day
Epichlorohydrin (ECH)	2263	1.07	107.0%	3rd
Epichlorohydrin (ECH)	1947	0.93	93.0%	4th

Table 6: 1.0ppb Check Standard and Percent Recovery

Conclusions

When dealing with drinking water analyses accuracy and precision are important due to the impact it can have on public health and safety. Detecting chemical impurities such as ECH, is critical to the water suppliers due to the tight restrictions placed on them by governing bodies. The European Normative 98/83/EC recommends limiting the concentration of ECH to 0.1ppb in water for human consumption. By using the Stratum PTC and AQUATek 100 autosampler with an Agilent 7890/5975 GCMS with SIM scan, ECH was precisely and accurately detected at 0.1ppb level (Figure 3). This allows for complete automation of the ECH analysis while still providing the sensitivity required by the European Normative 98/83/EC.

References

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