SPONSOR REPORT

Trace analysis of epichlorohydrin in drinking water using GC-MS coupled with purge and trap

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Keywords

Epichlorohydrin, volatile organic compounds (VOCs), drinking water, U.S. EPA, Purge and Trap (P&T), GC-MS, Helium Saver

Goal

Demonstration of an analytical method for the analysis of epichlorohydrin in drinking water down to 30 ppt using the Teledyne LABS Tekmar Lumin purge and trap (P&T) concentrator combined with the AQUATek LVA autosampler and the Thermo Scientific™ ISQ™ 7610 GC-MS for the analysis. Method linearity, method detection limit (MDL), precision, and mid-point calibration check were assessed to evaluate method performance.

Introduction

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 commonly used in the production of drinking water due to their durability and resistance to corrosion. However, ECH is known for its high reactivity and toxicity, which poses significant health risks if it contaminates drinking water. Exposure to ECH can cause respiratory issues, skin irritation, and has been classified as a probable human carcinogen.[1] Due to these risks, many countries have imposed strict limits on the amount of ECH allowed in drinking water. Recently, Europe set a minimum detection limit (MDL) of 30 parts per trillion (ppt) for ECH in drinking water.[2] Whereas typically required detection limits for most compounds mandated for analysis in Europe can be achieved using methods based on static headspace, the stringent MDL required for ECH requires preconcentration, for example using purge and trap (P&T) technology.[3,4] This technology involves purging the water sample with an inert gas to release volatile organic compounds (VOCs), which are then trapped and concentrated for analysis, ensuring reliable detection at very low concentrations. In the United States, the analysis of VOCs in drinking water is mandated by the Environmental Protection Agency (EPA). The EPA requires the use of P&T technology for drinking water analysis to ensure that even trace amounts of harmful compounds like ECH are detected and managed appropriately.

The following evaluation describes the use of the ISQ 7610 Single Quadrupole MS system coupled with the Thermo Scientific™ TRACE™ 1610 GC with the Thermo Scientific™ HeSaver-H_2Safer™ split/splitless injector and Teledyne LABS Tekmar Lumin P&T concentrator combined with the AQUATek LVA autosampler for the analysis of ECH in drinking water.

Experimental

Sample preparation

Three working calibration standards were prepared in methanol at concentrations of 100 parts per billion (ppb), 500 ppb, and 5 parts per million (ppm) from the following Restek™ standard: Epichlorohydrin Standard (P/N 30679).

A five-point linear (r^2) calibration curve was used from 30 to 5,000 ppt for all compounds utilizing Thermo Scientific™ vials (P/N C4013-2W) and cap and septum (P/N C4013-60A). The relative response factor (RRF) was calculated for ECH using the internal standard fluorobenzene. The internal standard was prepared in methanol from the fluorobenzene Restek standard (P/N 30030) at a concentration of 5 ppb, after which 5 µL was mixed with each 25 mL sample for a resulting concentration of 1,000 ppt.

Seven 30 ppt standards were prepared to calculate the MDL. Also, seven 1,000 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 Lumin P&T and AQUATek LVA conditions in Table 1.

Table 1. Tekmar Lumin P&T and AQUATek LVA water method conditions

Standby	Variable
Valve oven temp.	150 °C
Transfer line temp.	150 °C
Sample mount temp.	90 °C
Standby flow	10 mL/min
Purge ready temp.	35 °C
MCS purge temp.	20 °C
Purge	**Variable**
Purge temp.	20 °C
Purge time	11.00 min
Purge flow	100 mL/min
Dry purge temp.	20 °C
Dry purge time	0.00 min
Dry purge flow	100 mL/min
Sample heater enable	Off
Desorb	**Variable**
Desorb preheat temp.	175 °C
Desorb temp.	185 °C
Desorb time	2.00 min
Drain flow	300 mL/min
GC start signal	Begin Desorb
Bake	**Variable**
Bake time	2.00 min
Bake temp.	230 °C
MCS bake temp.	180 °C
Bake flow	200 mL/min
AQUATek LVA	**Variable**
Sample loop time	0.85 min
Sample transfer time	1.25 min

(continued)

Table 1 contd. Tekmar Lumin P&T and AQUATek LVA water method conditions

AQUATek LVA	Variable
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
Trap	1A
Chiller tray	On, 10 °C

GC-MS parameters

A TRACE 1610 GC was coupled to the ISQ 7610 MS equipped with the Thermo Scientific™ NeverVent ™ vacuum probe interlock (VPI) and an ExtractaBrite ion source. A Thermo Scientific™ TraceGOLD™ TG-VMS column, 30 m × 0.25 mm, 1.4 µm film (P/N 26080-3320) was used for compound separation. The HeSaver-H_2Safer SSL injector was utilized to reduce the carrier gas consumption by decoupling the gas used for the chromatographic separation from the gas used to pressurize the inlet and maintain split and purge flows. The critical separations were maintained with a run time of under 15 minutes. For this analysis, the ISQ 7610 MS was operated in Selected Ion Monitoring (SIM) mode for increased selectivity, as required for this application. Extended method parameters for the ISQ 7610 MS are shown in Table 2.

Table 2. GC-MS conditions

TRACE 1610 GC conditions	
Column	TraceGOLD TG-VMS, 30 m x 0.25 mm, 1.4 µm film; Helium carrier gas, 1.5 mL/min column flow
Oven profile	35 °C, 3 min 15 °C /min to 100 °C 25 °C/min to 240 °C 2 min hold Run time, 14.9 min
Inlet	HeSaver-H_2Safer SSL 200 °C, 20:1 split Purge flow, 5.0 mL/min 0.40 min helium delay
ISQ 7610 MS conditions	
Temp	Transfer line, 230 °C; Ion source, 280 °C
Mode	Timed-SIM
Scan	Fluorobenzene ions, *m/z* 96 Epichlorohydrin ions, *m/z* 57, *m/z* 49, *m/z* 62

Instrument control and data processing

Data was acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS). This software can control both the GC-MS system and the Tekmar Lumin P&T with the AQUATek LVA. This allows a single software to be utilized for the full workflow, simplifying the instrument operation. This application note is available for download via the Thermo Scientific™ AppsLab Library, which contains all the parameters needed to acquire, process, and report the analytical data for analysis of ECH.[5]

Results and discussion

Linearity and sensitivity

Using the parameters described in Table 2, excellent chromatography was achieved. The Tekmar Lumin P&T has an innovative Moisture Control System (MCS) that improves water vapor removal, thereby reducing peak interference and increasing GC column lifespan. Figure 1 displays consistent peak shape of a 30 ppt epichlorohydrin standard with minimal water interference.

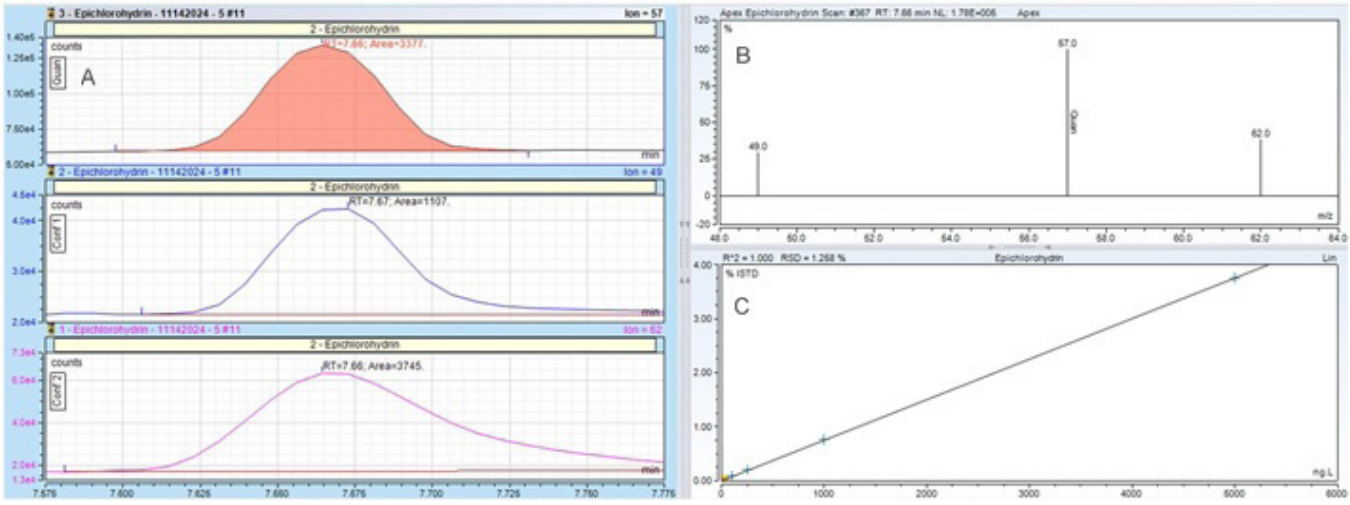

Figure 1. Chromeleon CDS results browser showing extracted ion chromatograms for ECH in the 30 ppt water standard, quantitation ion (*m/z* = 57) and two confirming ions (*m/z* = 49, *m/z* = 62) (A); a measured spectrum of ECH (B); and a linear calibration over a concentration range of 30 ppt to 5,000 ppt (C)

A calibration range of 30–5,000 ppt was evaluated. The calibration curve was used to calculate the response factor's average and relative standard deviation (%RSD), aiming for a %RSD of <20 to meet EPA criteria. The XLXR detection system of the ISQ 7610 MS, with its extended linear dynamic range and lifespan, enabled extended calibration curves and reduced replacement needs. The MDL was assessed using seven replicates of the 30 ppt standard. This data is shown in Table 3.

Method robustness

For use as a routine testing method, it is extremely important that the analytical method is stable and reproducible. To demonstrate this, 1,000 ppt standards (n=20) in water were injected at intervals over a 124-sample injection sequence. The samples were acquired with no user intervention at all on the P&T, GC or MS system and their concentrations were plotted to demonstrate the stability of the results. Figure 2 shows the reproducibility of epichlorohydrin over 124 injections with excellent percentage RSDs.

Reduced helium consumption and cost savings

The HeSaver-H_2Safer technology significantly extends helium cylinder lifetimes and offers substantial gas savings during idle periods and sample injection/analysis. Users can estimate its impact on helium consumption, cost, and cylinder lifetime using the Thermo Scientific™ Gas Saver Calculator tool.[6] By using this technology for epichlorohydrin analysis, the helium cylinder lifespan can nearly quadruple compared to a standard SSL injector, making it a prime choice for helium conservation. Figure 3 shows the helium saver calculator.

Table 3. Linearity, method detection limits, and mid-point calibration check

Compound	Calibration (30–5,000 ppt)			Method detection limits (n=7, 30 ppt)			Mid-point calibration check (n=7, 1,000 ppt)	
	RT	Ion	Linear ($r^2 \geq 0.995$)	MDL (ppt)	Precision (≤20%)	Accuracy (±30%)	Precision (≤20%)	Accuracy (±20%)
Fluorobenzene (IS)	6.27	96						
Epichlorohydrin	7.66	57	1.00	5	4.1	128	4.2	115

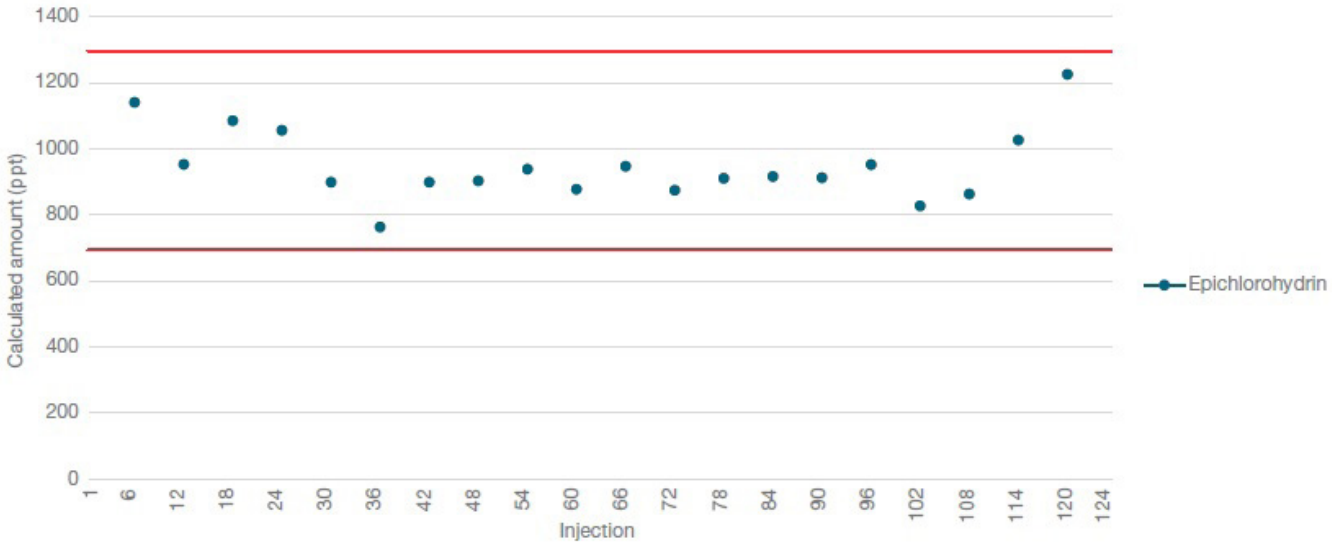

Figure 2. Reproducibility of epichlorohydrin at 1,000 ppt in water standards (n=20) over 124 injections

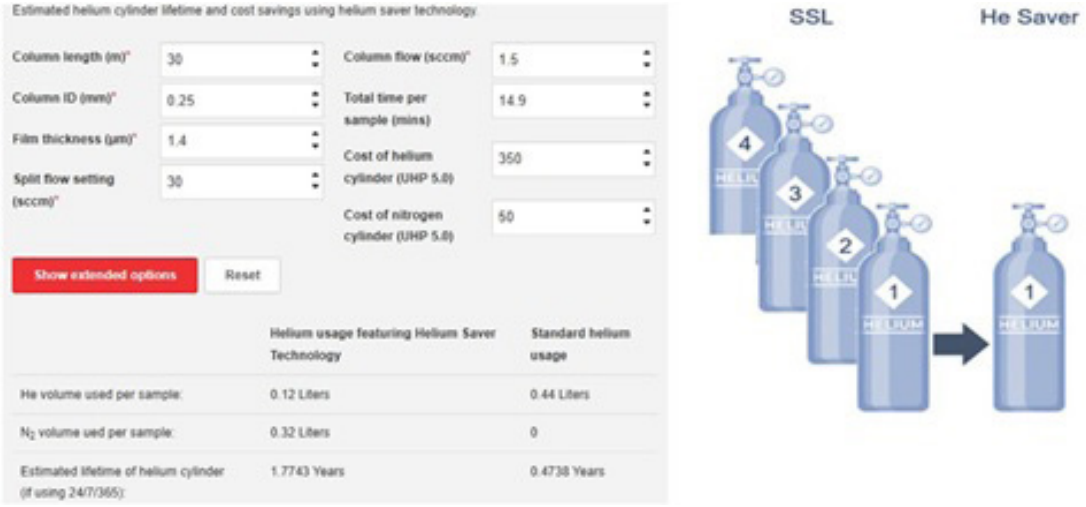

Figure 3. Helium saver calculator showing almost 4x savings of carrier gas

Conclusion

This study demonstrates the capability of the Tekmar Lumin P&T with the AQUATek LVA system connected to the ISQ 7610 Single Quadrupole GC-MS to detect and quantify low-level ECH in drinking water samples, in compliance with EPA requirements.

- Utilizing the Tekmar Lumin P&T's ability to purge with nitrogen, along with using the HeSaver-H₂Safer SSL injector, nearly four times less helium was consumed during the analysis without sacrificing system performance.
- The linearity of the calibration curve from 30 ppt to 5,000 ppt passed method requirements.
- The application proved robust during an extended study with 20 samples of a 1,000 ppt ECH standard injected over a series of 124 injections, obtaining 4.4% precision and 118% accuracy of the recovery.

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