Low-Level Analysis of Epichlorohydrin in Drinking Water by Headspace Trap-GC/MS

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Abstract

Epichlorohydrin, a raw material found in resins, can occur in drinking water at concentrations which are hazardous to human health. The use of epichlorohydrin is increasingly regulated. This article presents an analytical technique to determine the concentration of epichlorohydrin in drinking water, in response to the requirements of the European Normative 98/83/EC, which recommends limiting the concentration to a maximum of 0.1 µg/L.

The instrumental platform used for the low-level analysis of epichlorohydrin in drinking water was the PerkinElmer® TurboMatrix™ Headspace (HS) Trap coupled with a Clarus® 600 Gas Chromatograph/Mass Spectrometer (GC/MS). The use of headspace sample introduction allows trace detection of epichlorohydrin to be quantified in water without pre-treating the samples. The typical signal-to-noise determined for a sample fortified with epichlorohydrin at 0.1 µg/L is 114:1. The system was successfully calibrated across a working range of 0.1 to 50 µg/L with a linear calibration curve.

Introduction

Epichlorohydrin (1-chloro-2,3-epoxypropane) is a raw material used in the manufacture of various resins (epoxy resins, ion exchangers, etc.), elastomers, and glycerol and its derivatives. Epichlorohydrin-based polymers are used as a coagulant in the treatment of water supplies. The presence of epichlorohydrin in water is caused by its migration from various materials in contact with the water, into the water stream.

Resulting from the presence of a chlorine atom and an epoxy bridge, epichlorohydrin is highly reactive. The molecule will tend to hydrolyze when in contact with water at ambient temperature; hydrolysis is accelerated by heat or in the presence of an acid. The reaction between epichlorohydrin and certain alkali metals or alkali earth metals, such as iron and aluminum chlorides, as well as metal powders (zinc, aluminum, etc.), can be very violent or explosive.

Epichlorohydrin in drinking water has the potential to negatively impact human health. Studies carried out on rats established the LD50 (median lethal dose for 50% of the population) for oral administration of epichlorohydrin at 90 mg/kg. Additionally, it has carcinogenic properties: different types of tumors have been observed in rats and mice as a result of various administration routes and generally at high levels of exposure (tumors of the nasal fossae, subcutaneous sarcoma, stomach cancers, etc.).

Epichlorohydrin can enter the organism through a number of routes, including inhalation, skin contact, or ingestion. It causes depression of the central nervous system and skin irritation as well as irritation of the ocular and respiratory mucous membranes.

Because of the toxicity, inflammability and high reactivity of epichlorohydrin, strict preventive and protective measures have been mandated. The law restricting its application is the European Normative 98/83/EC concerning quality criteria for packaged water, special treatment and labeling for packaged mineral water and spring water, as well as spring water supplied in public taprooms.

This norm imposes a quality limit of 0.1 µg of epichlorohydrin per liter of water for packaged spring water and water made drinkable by treatment. The work presented here shows that the TurboMatrix HS Trap-Clarus GC/MS system will achieve the necessary 0.1 µg/L limit.

Experimental

The chromatographic conditions used in this analysis are described below.

TurboMatrix HS Trap

The fused-silica transfer line from the HS Trap is directly connected to the analytical column with a glass butt connector – this eliminates dead volume and transfers analytes to the GC without splitting or dilution. The complete HS conditions are presented in Table 1.

The TurboMatrix HS Trap allows for the analysis of samples without extensive sample preparation. The combination of the static headspace technique with a pre-concentration of samples on an adsorbent bed prior to injection makes it possible to reach low-level detection and quantitation limits.

Table 1. Analytical Configuration of the TurboMatrix HS Trap Sampler.

Trap Type:	Air Toxics
Oven Temperature:	70 °C
Needle Temperature:	160 °C
Transfer-Line Temperature:	170 °C
Trap Low Temperature:	30 °C
Trap High Temperature:	300 °C
Thermostat Time:	20 min
Vial Pressurization Time:	1 min
Desorb Time:	0.6 min
Dry Purge Time:	10 min
Injection Time:	0.3 min
Trap Hold Time:	10 min
Injection Mode:	Trap
Column Pressure:	25 psi
Vial Pressure:	29 psi
Desorption Pressure:	29 psi

Clarus 600 GC/MS

The chromatographic column used in this study was the PerkinElmer Elite-WAX™ column (60 m x 0.25 mm x 0.5 µm).

Helium was used as the carrier gas in both the GC and HS Trap; the HS Trap controls the pressure of the carrier gas at the column head at the specified pressure of 25 psi.

The GC injector-port temperature is set at 180 °C, 10 °C higher than the HS transfer-line temperature – this will prevent condensation of analytes in the injector port.

The GC oven program for this analysis is presented in Table 2 – the total run time was 16.5 minutes.

Table 2. Oven Program for Clarus 600 GC/MS.

Ramp Rate (°C/min)	Temperature (°C)	Temperature Hold Time (min)
–	80	1
5	150	1.5

The mass spectrometer method for this analysis utilized single ion and full ion scanning (SIFI) mode. SIFI collects both single ion monitoring data and full scan data simultaneously, ensuring accurate identification with full spectral data and enhanced sensitivity from the selected ion signal.

The calibration solutions used in this analysis were prepared in water with a series of dilutions from a stock solution. The stock solution was prepared at 50 ppb – this low-level solution reduces the exposure to excessively high concentrations of epichlorohydrin.

Results

In developing an analytical approach for the analysis of epichlorohydrin in drinking water, a medium-level calibration standard was analyzed in full-scan mass spectral acquisition to determine the retention time of the analyte and to gather experimental spectral data for the development of a SIFI acquisition method.

Figure 1 demonstrates the chromatographic peak of an epichlorohydrin standard at 1 ppb. The measured retention time of epichlorohydrin under the conditions presented in this study is 10.46 minutes. In Figure 1, the bottom (red) chromatogram is the trace obtained in full scan mode, and the top (green) chromatogram is the trace obtained in single ion recording (SIR) mode.

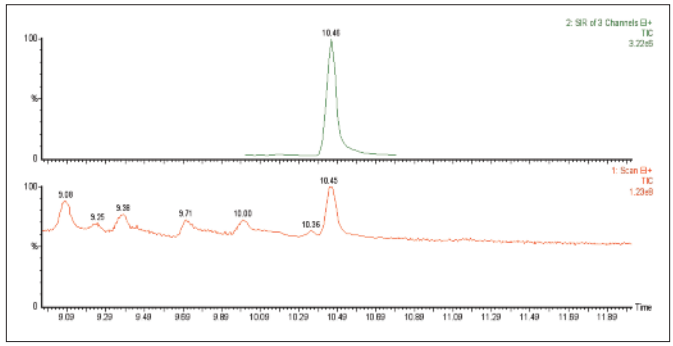

Figure 1. Chromatogram obtained for the analysis of epichlorohydrin at 1 µg/L in both full scan and SIR acquisition modes.

The mass spectral data from the full scan analysis of a 1-µg/L standard of epichlorohydrin in water is shown in Figure 2.

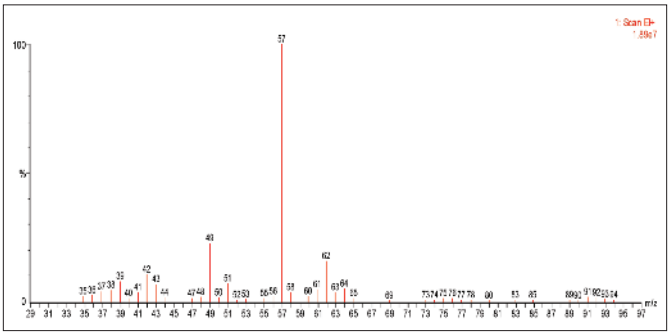

Figure 2. Mass spectrum obtained for the analysis of epichlorohydrin at 1 µg/L in full scan mode.

The spectrum in Figure 2 shows the molecular mass at m/z 92. Additionally, characteristic masses are measured at m/z 62, m/z 57 and m/z 49. In the SIFI MS method, m/z 57 will be used for quantification and the ions m/z 62 and m/z 49 will confirm the identification of the analyte.

For 1 ppb of epichlorohydrin in water, the SIFI analysis resulted in a signal-to-noise of 1200:1 in SIR mode. This analysis was followed with the analysis of a 0.1-ppb solution, resulting in a 114:1 signal-to-noise ratio. The resulting chromatogram for both full scan and SIR analysis of 0.1-ppb epichlorohydrin in water is shown in Figure 3. This method is easily able to reach and exceed the detection and quantification limits required by law.

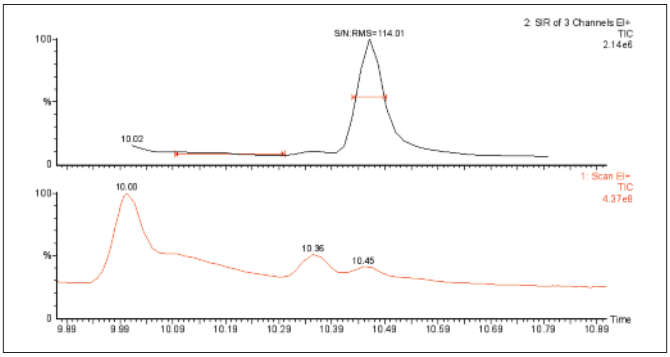

Figure 3. Chromatogram obtained in SIFI mode for 0.1-µg/L solution.

Once the sensitivity of the method and analytical system were verified, a study to determine the linear calibration range of the method was performed. Table 3 shows the concentration range used in this study.

Table 3. Concentration Range Used to Study the Linearity of the Response.

	Concentration	No. of Injections
Solution 1	0.1	3
Solution 2	1	3
Solution 3	5	3
Solution 4	10	3
Solution 5	50	3

Figure 4 demonstrates the graphical representation of the response and calibration curve for epichlorohydrin.

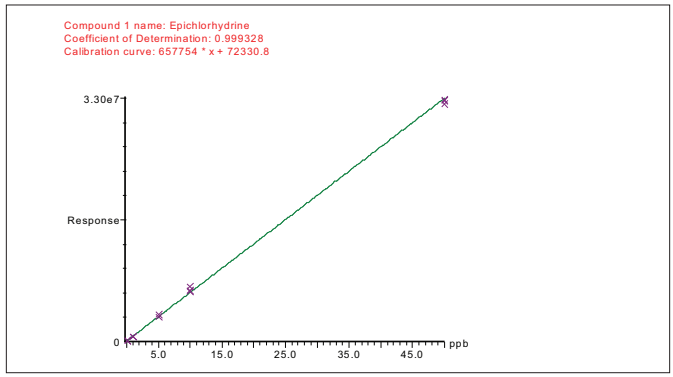

Figure 4. Calibration curve obtained for the analysis of epichlorohydrin.

The working range for this analysis was determined to be from 0.1 through 50 ppb with very good linearity, as represented by a correlation coefficient of 0.9993.

The low point of calibration required by law is 0.1 ppb. To verify that this level is both precise and accurate with the analytical method presented here, a repeatability test was performed. Six duplicate samples fortified at 0.1 ppb were consecutively analyzed. The results presented in Table 5 (Page 4) show that the area of the peak is reproducible, verifying precision. The concentration calculated from the previous calibration curve demonstrates that the analysis of a fortified sample results in the reporting of the expected concentration, verifying the accuracy.

Table 5. Analysis-Repeatability Test on Six Samples of Epichlorohydrin at 0.1 µg/L.

	Retention Time	Area	Calculated Concentration
Solution 1	10.46	137644	0.099
Solution 2	10.46	137702	0.099
Solution 3	10.46	141268	0.105
Solution 4	10.46	138587	0.101
Solution 5	10.46	139429	0.102
Solution 6	10.46	137157	0.099
Mean	10.46	138631	0.099
RSD	0%	1.01%	2.17%

Conclusion

This study has shown that the combination of the TurboMatrix HS Trap with the Clarus 600 GC/MS is an excellent instrumental platform for the low-level analysis of epichlorohydrin in water. This system virtually eliminates sample preparation by using headspace sample introduction. The application of adsorbent-trapping technology concentrates the headspace and provides the sensitivity needed to exceed the low-level threshold required by the latest regulations.

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