Trace Level Analysis of Epichlorohydrin in Drinking Water by Gas Chromatography/ Flame Ionization Detector

Application Note

Gas Chromatography/Environmental

Author

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Abstract

A rapid, economic, sensitive and reliable method for the determination of epichlorohydrin (ECH) in drinking water is presented. After extraction by methylene chloride, trace-level ECH was quickly concentrated with K-D concentrator. An Agilent 7890A GC System with an Agilent J&W DB-5ms Ultra Inert column were used for ECH analysis. The calibration curves were linear over the range of 0.08–1.60 ng with correlation coefficients greater than 0.9997. Recoveries of ECH at spiked levels of 1.0, and 5.0 µg/L were 104.7% and 107.0%, respectively. The RSD value for ECH reproducibility was lower than 2.21%. The detection limit was less than 0.07 µg/L, which is below the maximum residue limit (MRL) of 0.1 µg/L in European Union regulations for ECH in drinking water.

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Introduction

Epichlorohydrin (ECH), 1-chloro-2,3-epoxypropane, is a raw material used in the production of epoxy resins, synthetic glycerol, elastomers, paper, and pharmaceuticals [1-2]. ECH can enter drinking water supplies by leaching from epoxy resin coatings on pipes or through flocculating agents in water treatment. As a result of its widespread use, low concentrations of ECH in wastewater, ground water and surface water have been observed. Toxicological studies show that ECH has severe acute and chronic toxic effects on humans. Therefore, ECH is listed among chemicals that must be monitored because of its effect on human health. According to the European Council Directive 98/83/EC on the quality of waters intended for human consumption, its acceptable limit in drinking water is 0.1 µg/L [3].

The main analytical methods available for epichlorohydrin quantification in water include gas extraction techniques, such as static headspace (HS), dynamic headspace – purge and trap (P&T) GC with mass spectrometric, flame ionization, or electron-capture detection. L. Lucentini, and colleagues [6] developed a method based on GC-ECD for ECH in drinking water samples with static headspace (LOD = 40µg/L) and purge and trap (P&T) (LOD = 0.01 µg/L). The LOD (40 µg/L) for static headspace cannot meet the EU regulation requirement. P&T is a sensitive, simple and rapid method; however, it requires some automatic equipment, which makes it an expensive option.

A method for ECH determination by ion chromatography has been developed. The technique is based on the reaction between an analyte and sulfur (IV) to form a product with a terminal sulfonate group that can be analyzed by anion-exchange chromatography [7,8]. The method (LOD = 0.07 µg/L) is, however, cumbersome and time consuming and requires a derivatization step.

An economic, reliable, sensitive, and robust analytical method is needed for the analysis of ECH in drinking water samples (LOD<0.1 µg/L). The problem with the analysis of ECH in water samples arises from its high solubility in water (66 g/L), volatility and polar character [4]. In this application, a classical extraction technique, liquid-liquid extraction followed by K-D concentration was used for the sample preparation. Compared with other concentrate techniques, K-D concentrator is suitable for evaporating the solvent with less analyte loss.

Column inertness is crucial for the analysis of active compounds such as ECH. If a column lacks inertness, it will exhibit severe peak tailing, and response loss leading to inaccurate quantification. The Agilent J&W Ultra Inert column has the most consistent column inertness. It gives better sensitivity and peak shape for active compounds and reliable results for trace level analysis. In this paper, a 10-m length minibore, 0.18 mm id capillary Agilent J&W DB-5ms Ultra Inert column was used to determinate ECH in drinking water by GC/FID.

Experimental

Instrument

An Agilent 7890A GC System equipped with a split/splitless capillary inlet and flame ionization detector (FID) was used for this work. The split/splitless inlet was fitted with a long-lifetime septa (p/n 5183-4761) and split liner (single taper, p/n 5183-4647). Injections were done using 10 µL syringes (p/n 9301-0714).

Table 1. Gas Chromatography Conditions

Column	Agilent J&W DB-5ms Ultra Inert, 10 m*× 0.18 mm, 0.36 µm (p/n 121-5523UI)
Carrier Gas	Helium, constant flow mode, 1.5 mL/min
Inlet	Pulsed split 24.6 psi at 250 °C, split 5:1
Oven Temp	30 °C (1 min); 20 °C/min to 100 °C (2 min)
Detector	FID at 260 °C
Detector Gas	H_2 30 mL/min, air 400 mL/min, makeup (N_2) 25 mL/min
Injection Size	4 µL

*The 10-m length capillary column was cut from a 20-m length column.

Standard solution

ECH stock solutions (1000 mg/L) in methanol were purchased from China National Standards Research Center. Five calibration standard solutions were prepared by diluting the stock solution with methylene chloride. The calibration standard solutions were stored in tightly sealed bottles below 5 °C.

Sample preparation

A 200 mL amount of water sample and 10 g sodium chloride (NaCl) were transferred into a 500-mL separatory funnel. After complete disolution of NaCl, 10 mL of methylene chloride were added. The separatory funnel was sealed and then shaken vigorously for 1–2 minutes with periodic venting to release excess pressure. After the funnel was still for 10 minutes, the extract for the organic layer was collected. The extraction was repeated twice using fresh portions of solvent. The resulting three portions of the extracts were combined into a K-D tube. The K-D tube was quickly placed in a K-D concentrator to evaporate the solvent to near dryness. The residue was dissolved with 1 mL of methylene chloride and transferred into the sample vial for GC analysis.

Results and Discussion

Figure 1 shows the chromatogram of ECH (0.08 ng on-column). As illustrated, on the 10-m length (0.18 mm id) DB-5ms Ultra Inert capillary column, ECH can be eluted from the column in less than 2 min, with a symmetrical peak shape.

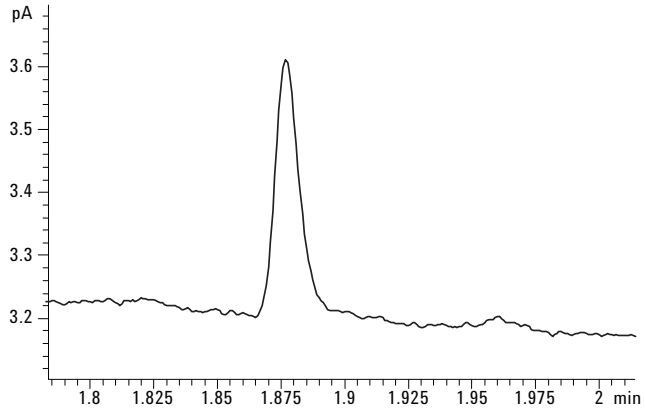

Figure 1. Chromatogram of ECH on an Agilent J&W DB-5ms Ultra Inert column.

Linearity

Figure 2 shows the calibration curve for ECH in the study. It was constructed from data obtained from five levels of standards. ECH exhibits a wide linear range from 0.08 ng to 1.60 ng with r^2 value higher than 0.9997.

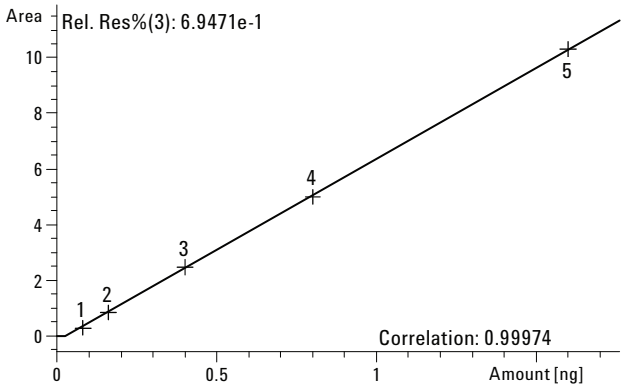

Figure 2. Calibration curve for ECH.

Recovery and Limit of Detection (LOD)

Table 2 presents the recoveries for spiked water samples. Blank samples of 200 mL were spiked with ECH at 1 µg/L and 5 µg/L. During the study, the local drinking water was free from ECH contamination, and the analysis had no impurity interferences (Figure 3). It was regarded as a blank sample. The spiked samples were treated according to the procedure described in the sample preparation. Excellent recoveries were obtained, with the average values of 104.7% and 107.0%. Figure 4 shows the triple analysis of 1 µg/L spiked water samples with good reproducibility and RSD at 2.21%.

Table 2. Recovery and Reproducibility of the Method

	Recovery (%)	
	1 µg/L	5 µg/L
1	102.0	106.8
2	106.2	104.9
3	105.8	109.2
Avg	104.7	107.0
RSD (%)	2.21	2.01

The Limits of Detection were determined at a signal-to-noise ratio of 3. The developed method enables quantitative determination of ECH in water solutions at concentration levels lower than 0.07 µg/L, which is lower than the MRL of the European Union (0.1 µg/L) in drinking water.

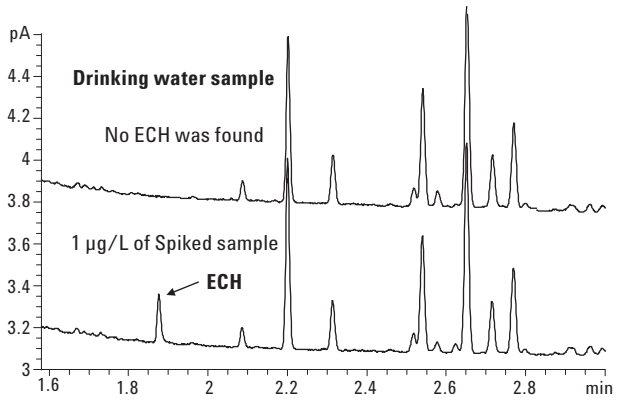

Figure 3. Comparison of blank sample and 1 µg/L of spiked sample.

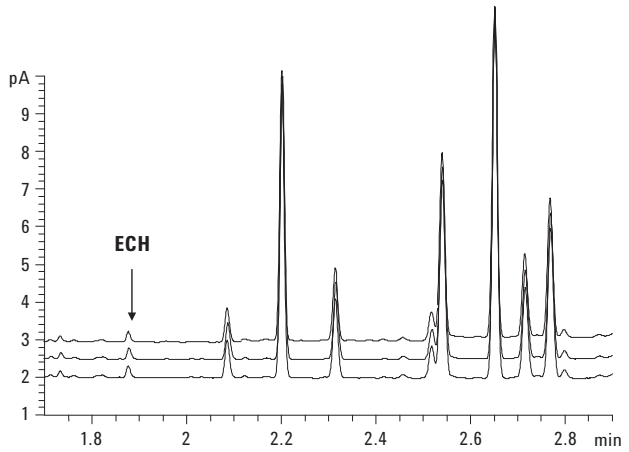

Figure 4. Triple analysis of 1 µg/L of spiked sample.

Conclusions

This application describes a rapid, economic, sensitive and reliable method for the quantification of trace level ECH in drinking water samples. The method provides good linearity, repeatability, and high recovery. It is applicable for determining ECH at trace levels in drinking water. It is also useful for routine laboratory activities, both for control and research.

Reference

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