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Determination of epichlorohydrin by ion chromatography

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Abstract

In this work we developed a new method for epichlorohydrin determination with suppressed ion chromatography. The technique is based on a reaction between the analyte and sulfur(IV) to form a product with a terminal sulfonate group that can be analyzed by anion-exchange chromatography. The reaction conditions were optimized as a function of temperature, type and concentrations of reagents and pH. Due to the characteristics of the product formed, the columns used were an IonPac AS11 and AS11-HC with a NaOH eluent. The eluent concentration was optimized in order to achieve a complete separation of epichlorohydrin, chloride and nitrate ions, commonly occurring in drinking waters. In order to improve the detection limits, a preconcentration step, using reversed-phase materials, has been optimized. The method developed was suitable for epichlorohydrin determination in drinking water.

Keywords: Kinetic studies; Water analysis; Epichlorohydrin

1. Introduction

Epichlorohydrin (also chloromethyl-ethylene oxide, chloromethyl oxirane or glycidyl chloride) is an organic liquid with a garlic-like odor. It is mainly used for production of glycerin, plastics, polymers, some of which are designed for water supply systems. Epichlorohydrin finds applications in the paper and drug industries and as an insect fumigant [1]. Due to its use as a clarifier in water treatment, through coagulation and trapping of suspended solids, epichlorohydrin presence is a concern for drinking waters. If complete coagulation does not occur, epichlorohydrin can be found in drinking waters.

Exposure to epichlorohydrin at levels above the maximum contaminant level (MCL) for relatively short periods of time can damage skin, liver, kidneys and the central nervous system. Lifetime exposure can also cause chromosome aberration and cancer. The MCL goal for epichlorohydrin has been set at zero by the US Environmental Protection Agency (EPA), in order to avoid health risks previously listed [1].

Due to its toxicity, epichlorohydrin has been listed among compounds dangerous to the water environment. No acceptable means of detecting epichlorohydrin are currently available and the EPA requires water suppliers to use special treatment techniques to control its release into the environment [1].

Literature methods for the determination of epichlorohydrin in water samples are based on gas chromatography (GC) preceded by time-consuming and poorly reproducible headspace [2] or liquid–liquid [3] extraction enrichment. Recently, an analytical method based on solid-phase extraction and subsequent GC determination has been presented [4]. To our knowledge, no liquid chromatographic meth-

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od is available for the determination of epichlorohydrin.

The aim of this work was to develop a reliable technique for epichlorohydrin determination based on liquid chromatography. The analytical determination is performed on the products of a nucleophilic attack of the epoxide ring by S(IV). Since reaction products are strongly ionized anions, the separation has been performed on a anion-exchange columns with NaOH eluents. Detection has been reached by suppressed conductivity. The method has been optimized through the parameters involved in the derivatization reaction. The method developed, coupled with a preconcentration procedure, allowed one to obtain, after procedure optimization, a detection limit of 70 ng/l epichlorohydrin.

2. Experimental

2.1. Chromatographic system

The apparatus consisted of a Model QIC ion chromatograph (Dionex, Sunnyvale, CA, USA) equipped with a single-piston DQP pump. The volume of the sample loop was 200 μl. The analytical columns included the guard columns IonPac AG11, AG11-HC (50×4 mm I.D.) and the separator columns IonPac AS11 and AS11-HC (250×4 mm I.D.) from Dionex. Measurements with AS11-HC were performed with a GP50 gradient pump coupled to the EG40 eluent generator (Dionex).

The resin of the AS11 columns is composed of 13 μm polystyrene–divinylbenzene substrate agglomerated with a completely aminated anion-exchange latex. The ion-exchange capacity is approximately 45 μequiv./column. The AS11-HC column has a super macroporous substrate with a 2000 Å pore diameter and high capacity (290 μequiv./column) with selectivity similar to the AS11 column.

For preconcentration measurements disposable cartridges, OnGuard-RP (Dionex) containing macroporous polystyrene–divinylbenzene resin were used. For sample pretreatment (chloride ion removal), OnGuard-Ag (Dionex) cartridges were used. Eluent solutions contained NaOH at proper concentration. Unless otherwise stated, eluent flow-rate was set at 1 ml/min. Detection was achieved by a conductivity detector. Eluent conductivity was suppressed by an Anion MicroMembrane Suppressor (AMMS-II). The regenerant solution was a 25 m*M* sulfuric acid solution. With the GP50 and EG40 system, a Self-Regenerating Suppressor (SRS) from Dionex was used. A chromatographic data system (AI-450, Dionex) was used for data collection and processing. Chromatograms were recorded at room temperature. Retention times represent the average values of at least three injections. Dead volume, 1.8 ml, was evaluated by the negative peak due to water.

2.2. Reagents and solutions

(±)-Epichlorohydrin, anhydrous sodium sulfite and methanol were from Fluka (Buchs, Switzerland), sodium hydroxide, anhydrous sodium sulfate and ethanol were from Merck (Darmstadt, Germany).

All aqueous solutions were prepared using high-purity water obtained with a Milli-Q system (Millipore, Bedford, MA, USA). Eluents were filtered through 0.22-μm filters before use.

3. Results and discussion

Derivatization of epichlorohydrin was performed by ring opening with sulfite ion, according to the reaction detailed in Fig. 1 [5]. Great disagreement exists about the product of the sulfur(IV)–epichlorohydrin reaction. A product with a normal terminal sulfonate group has been reported [5], but

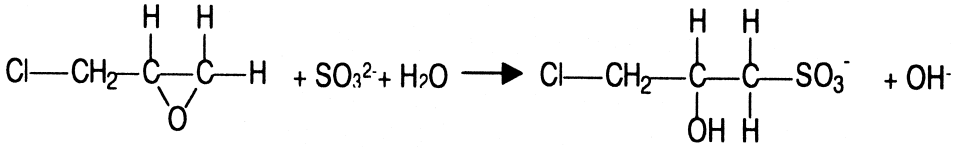

Fig. 1. Reaction between sulfur(IV) and epichlorohydrin.

the reaction has also been reported to give under some conditions terminal sulfonate by replacement of the chloride, without disturbing the ring [6]. However, this last report has been questioned [5]. The nuclear magnetic resonance (NMR) spectra of epichlorohydrin with excess sulfite and ^2H_2O solution apparently include at least two organic species [6], but they are not consistent with complete conversion to any one of the three expected products (1-chloro-2-hydroxy-3-propanesulfonic acid [5], 1-chloro-3-hydroxy-2-propanesulfonic acid or 1,2-epoxy-3-sulfonic acid [6]).

3.1. Choice of preliminary reaction conditions

The reaction was preliminary carried out in 10 m*M* NaOH, 50% water ethanol and 2.3 m*M* Na_2SO_3 with increasing concentrations of epichlorohydrin. It has been shown [7] that under these reaction conditions, using an epichlorohydrin concentration of 4.9 m*M*, the rate reaction was first order in sulfite and was about 0.02 M^{-1} s^{-1}.

The evaluation of reaction products and further experiments, unless stated otherwise, was performed by ion chromatography (IC) using the IonPac AG11 and AS11 columns with a 5 m*M* NaOH eluent solution, after 1:10 dilution in 50% water ethanol. Due to the solubility of epichlorohydrin in water (especially at low concentrations), the same reaction has been even performed without ethanol.

The chromatograms obtained show for both reaction media, the presence of two peaks for epichlorohydrin at 2.06 and 2.50 min, of increasing height and area for increasing concentration of epichlorohydrin. The two peaks are probably due to the formation of the two species – 1-chloro-2-hydroxy-3-propanesulfonic acid, 1-chloro-3-hydroxy-2-propanesulfonic acid [5] – that can be easily detected by conductivity. Due to steric effects, the attachment of the sulfite ion at the carbon atom carrying the chloride substituent is difficult.

Since the method had to be optimized mainly for determination of epichlorohydrin in water samples, further experiments have been performed in aqueous media, without further addition of ethanol.

Preliminary experiments evidenced that the chromatographic peaks of the two species of epichlorohydrin (arbitrarily named in this work as Epi1 and Epi2) did not increase with epichlorohydrin concentration. These results indicated that reaction is sensitive to analysis time conditions, therefore, further experiments were performed injecting derivatized solutions after 24 h of reaction. As an example, Fig. 2 shows the chromatogram of $8.56 \cdot 10^{-4}$ *M* epichlorohydrin obtained 24 h after reaction with sodium sulfite and NaOH.

Under these conditions, relative standard deviation (RSD) ($n=4$) values were 45.1% for Epi1 and 41.9% for Epi2. Due to the high RSD values obtained, reaction has been performed at controlled reaction temperature conditions, and its kinetics studied.

3.2. Kinetics of the reaction in NaOH

The kinetics were studied for 240 h at 30°C with a 10 m*M* NaOH, 2.3 m*M* Na_2SO_3 and $4.4 \cdot 10^{-4}$ *M* epichlorohydrin solution. In parallel, a blank solution was prepared and processed in the same way. After reaction, for each time studied, the solution was diluted 1:10 with water before injection. Results show that epichlorohydrin peak area reaches a maximum value reaction after 24 h and that after this time, it does not show any significant increase. After 9 days reaction, the species labeled as Epi1 degrades originating a new peak at 1.90 min. The linearity of

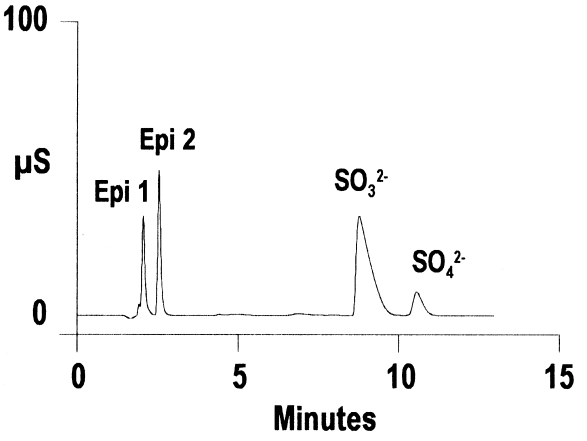

Fig. 2. Chromatogram of derivatized epichlorohydrin with sulfur(IV). Reaction conditions: $8.56 \cdot 10^{-4}$ *M* epichlorohydrin, 10 m*M* NaOH, 2.3 m*M* Na_2SO_3. Reaction performed at ambient temperature. Column: IonPac AS11 (250×4 mm I.D.). Eluent 5 m*M* NaOH. Eluent flow-rate: 1 ml/min. Detection: suppressed conductivity.

the epichlorohydrin species and standard deviation of the reaction have been evaluated after 24 h for the following solutions containing 1.3, 2.2, 4.4 and $8.6 \cdot 10^{-4}$ *M* epichlorohydrin. Standard deviations ranged from 1.3 to 9.6%, while regression coefficients r^2 were 0.998 and 0.997 for the two peaks of epichlorohydrin, respectively.

In order to verify the effect of temperature on the kinetics, the reaction was also performed at 80°C. This temperature was chosen in order to keep it below the boiling temperature (115°C). Solutions of epichlorohydrin were injected at increasing reaction times. Results indicated that at 80°C, the reaction is completed after 1 h, but its yield is lower than that obtained after 24 h at 30°C, therefore, these conditions were subsequently chosen for further experiments. In order to evaluate the suitability of the system for lower epichlorohydrin level concentrations, the following solutions were prepared at 1.3, 2.5, $3.7 \cdot 10^{-5}$ *M*, 1:10 diluted in water and injected. The regression coefficients for the two epichlorohydrin peaks were $r^2_{\text{Epi1}}=0.997$ and $r^2_{\text{Epi2}}=0.909$, with a blank interference of NaOH solution for the first epichlorohydrin peak. Considering the applicative purpose of the method (water analysis) and the interference of NaOH solution, we evaluated the yield of reaction performed without NaOH solution.

3.3. Kinetics of the reaction in water

In order to compare the reaction performance, the same experimental conditions were used. Therefore, kinetics were studied for 240 h at 30°C with a 2.3 m*M* Na_2SO_3 and $4.4 \cdot 10^{-4}$ *M* epichlorohydrin solution and a blank. After reaction, the samples were diluted 1:10 with water before injection. Results shown in Fig. 3 indicate that after 24 h the reaction is complete and epichlorohydrin peak areas do not significantly increase any further. In tandem, a decrease of sulfite peak area has been noted with increase of reaction time.

The yield of reaction in water for the two peaks of epichlorohydrin is 52 and 72% of those obtained with NaOH, respectively. The efficiency of reaction in NaOH is higher because basicity favors the opening of the epoxydic ring by the sulfite ion. Although the yields in water are lower, the following experiments were performed in water due to the lower risk of introduction of contaminations and for the lack of interference with the epichlorohydrin peak. Moreover, after 24 h a better stability of the epichlorohydrin peaks was evidenced without NaOH. Under these conditions linearity and reproducibility of the reaction was evaluated at the following epichlorohydrin concentrations: 1.3, 2.2, 4.4 and $8.6 \cdot 10^{-4}$ *M*. Each epichlorohydrin concentration was prepared in five sets. Solutions after reaction at 30°C for 1 h were diluted 1:10 and injected into the chromatographic system. Standard deviations were lower than 8.0% ($n=5$) and regression coefficients for the two peaks were $r^2=0.993$ and 0.999. As expected, the peaks for epichlorohydrin did not present any interference from the blank.

In order to reduce epichlorohydrin level concentrations, the reaction has also been performed at 2.5, $5.1 \cdot 10^{-6}$ *M* and 1.0, $1.3 \cdot 10^{-5}$ *M*. At these lower epichlorohydrin concentrations, quantitative analysis has only been performed for the peak labeled Epi2.

3.4. Effect of sodium sulfite concentration

Reaction of epichlorohydrin at concentrations of 1.0 and $1.3 \cdot 10^{-5}$ *M* was performed at 30°C with a different sodium sulfite concentration (Fig. 4). For each epichlorohydrin and sodium sulfite concentration, three sets of solutions have been prepared and injected. At 0.23 m*M* reagent concentration is not sufficient to provide the epichlorohydrin derivatization, not even after 48 h of reaction. At 10 m*M* sodium sulfite concentration, although standard deviations are very low (2.0%, $n=3$), epichlorohydrin peak is not baseline resolved from species present in blank solution eluted at the void volume. At 6.0 m*M* standard deviations are still good (2.4%, $n=3$) and epichlorohydrin peak is resolved enough for a quantitative determination.

According to the experimental results obtained, a concentration of 6.0 m*M* has been considered optimal for epichlorohydrin derivatization.

3.5. Reproducibility and detection limits

After optimization of the reaction conditions, derivatization has been performed with three differ-

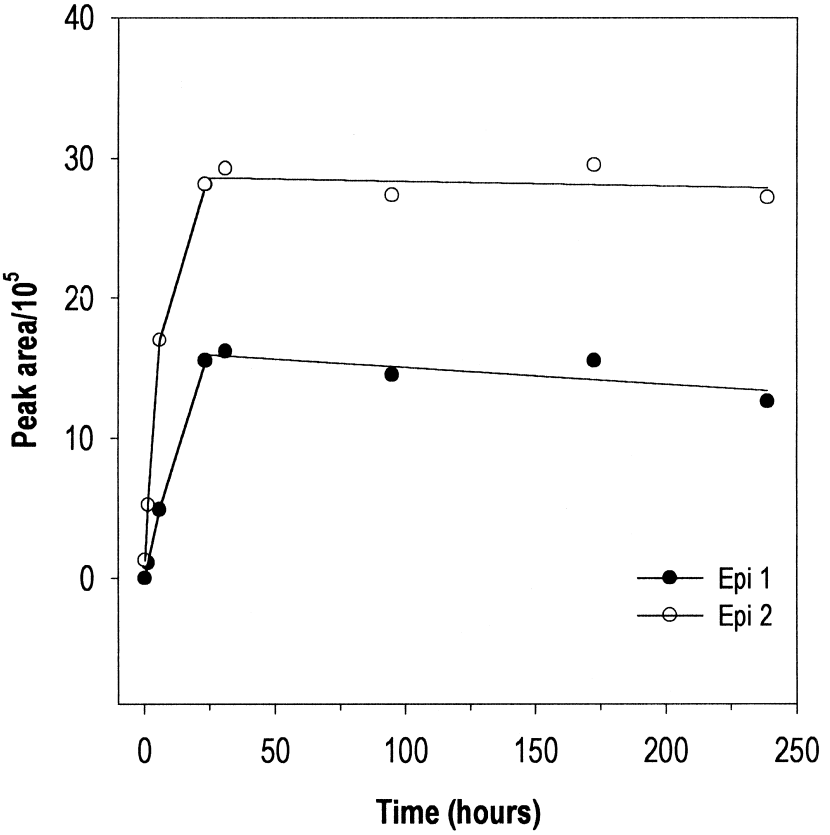

Fig. 3. Study of the kinetics for epichlorohydrin derivatization. Reaction conditions: 30°C, 2.3 m*M* Na_2SO_3 and $4.4 \cdot 10^{-4}$ *M* epichlorohydrin. Chromatographic conditions as in Fig. 2.

ent solutions containing epichlorohydrin at concentrations of $2.5 \cdot 10^{-6}$ *M* (235 ppb) and three other solutions of $5.1 \cdot 10^{-6}$ *M* (470 ppb) epichlorohydrin. Sodium sulfite concentration was kept at $6.0 \cdot 10^{-3}$ *M*, as previously optimized. A blank containing only $6.0 \cdot 10^{-3}$ *M* sodium sulfite was also prepared. After 24 h of reaction at 30°C, blank and epichlorohydrin solutions were diluted 1:1 with water and injected. Fig. 5 shows the chromatograms for the blank and for 470 ppb epichlorohydrin. Standard deviations of the method are 7.7% for $2.5 \cdot 10^{-6}$ *M* and 5.4% ($n=3$) for $5.1 \cdot 10^{-6}$ *M* epichlorohydrin. Due to the blank signal, the detection limit for epichlorohydrin determination, evaluated as three-times the noise signal, was calculated after subtraction of the blank peak. The value found was 0.6 ppb.

3.6. Preconcentration in ultrapure and drinking waters

A preconcentration procedure was first developed in ultrapure water and then applied to drinking water analysis.

The preconcentration substrate was an OnGuard-RP cartridge containing macroporous divinylbenzene resin which has a very high selectivity for hydrophobic substances. Before each experiment, the cartridge was conditioned with 5 ml CH_3OH and 10 ml water. First preconcentration experiments were performed flowing a 20 ml solution containing 470 ppb epichlorohydrin through the cartridge. In order to verify that epichlorohydrin was completely retained by the cartridge, waste was collected. Succes-

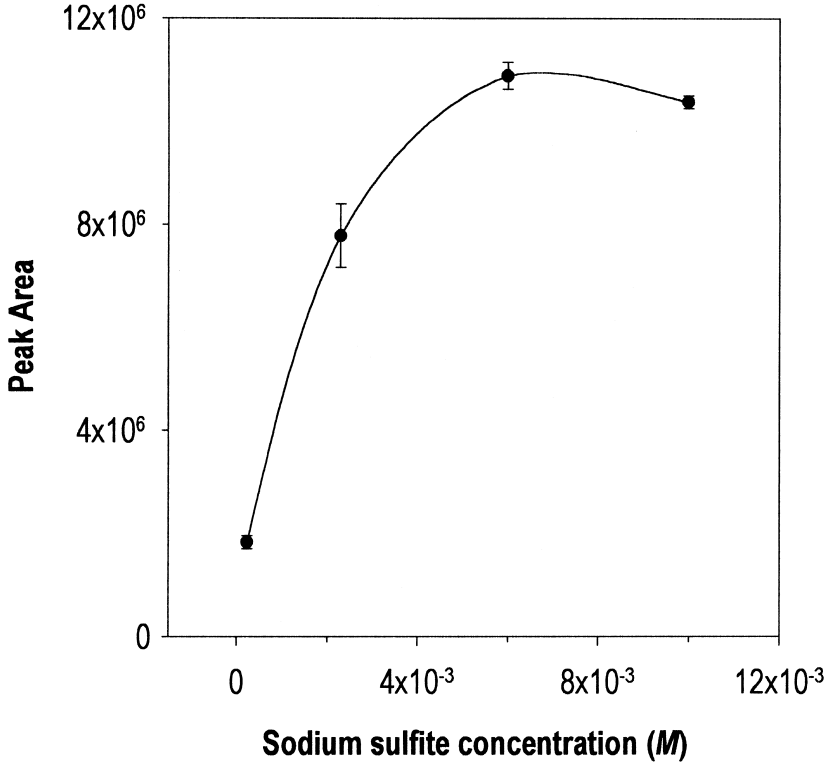

Fig. 4. Effect of sodium sulfite concentration on the yield of reaction. Epichlorohydrin concentration $1.3 \cdot 10^{-5}$ *M* (1.17 ppm). Reaction temperature: 30°C. Chromatographic conditions as in Fig. 2. Error bars represent the standard deviations calculated from triplicate injection of three sets of the same sodium sulfite and epichlorohydrin concentration.

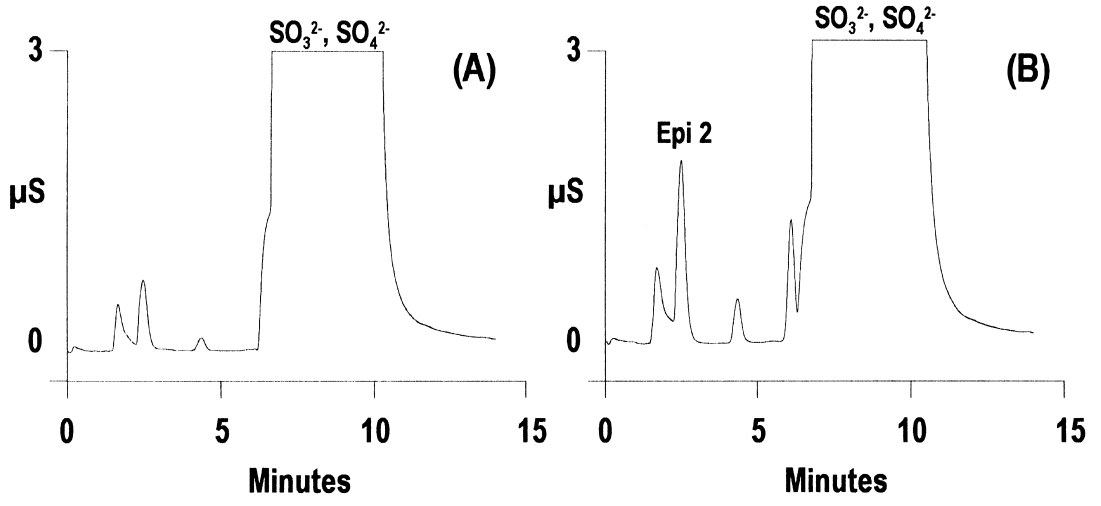

Fig. 5. Determination of epichlorohydrin by the optimized reaction conditions (6 m*M* sodium sulfite, 24 h at 30°C). Chromatographic conditions: column IonPac AS11, eluent: 5 m*M* NaOH. (A) Blank solution, (B) $5.07 \cdot 10^{-6}$ *M* epichlorohydrin.

sively, 10 ml of CH_3OH–water (50:50, v/v) was used to elute epichlorohydrin from the OnGuard cartridge (preconcentration factor 2). Eluates obtained after preconcentration and wastes were reacted for 1 h at 30°C with $6.0 \cdot 10^{-3}$ *M* sodium sulfite. After reaction of eluates and wastes, solutions were diluted 1:1 with water and injected into the chromatographic system. The chromatogram obtained for the eluate is shown in Fig. 6. The recovery calculated by comparison with the same nominal amount of epichlorohydrin without preconcentration is 96.1±5.8%. The high recovery, i.e., the complete retention of epichlorohydrin by the cartridge, was verified through injection of the waste. The chromatogram obtained showed that epichlorohydrin is present below the detection limit of the method.

In order to reduce the level of the epichlorohydrin concentration detectable, experiments were performed at a preconcentration factor 10. In fact, 60 ml of water containing 94 ppb of epichlorohydrin was flowed through an OnGuard-RP cartridge, activated as previously detailed, and eluted by 6 ml of water–methanol (1:1). The eluate was reacted with sodium sulfite under the conditions previously optimized. Under these conditions, a recovery of 88.3±8.1% was achieved. The effects of methanol medium in the yield of reaction have been also investigated. A

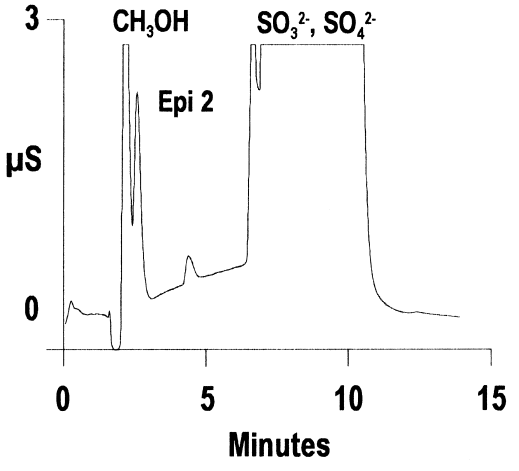

Fig. 6. Preconcentration of 470 ppb epichlorohydrin. Reaction and chromatographic conditions as in Fig. 5. Preconcentration procedure: 20 ml of epichlorohydrin solution preconcentrated on the cartridge OnGuard-RP and eluted by 10 ml water–methanol (50:50, v/v) mixture.

1-ppm amount of epichlorohydrin, reacted for 1 h at 30°C in $6.0 \cdot 10^{-3}$ *M* sodium sulfite in water–methanol (1:1) and in pure water, was diluted 1:1 with water. The comparison of the two chromatograms obtained evidenced that the derivatization reaction has the same yield for both media.

The method developed was applied to the determination of epichlorohydrin in a drinking water sample. Before analysis, drinking water was filtered through 0.22-μm filters and then passed through OnGuard-Ag cartridges for elimination of chloride ions interference. In fact, as evidenced throughout the experiments, the peak of the chloride ion can interfere with that of epichlorohydrin. Samples were added with known amounts of epichlorohydrin, 1:10 preconcentrated and eluted with the methanol–water solutions. Then eluates were derivatized as optimized, diluted 1:1 with water and injected into the chromatographic system. Fig. 7 shows an example for a drinking water sample, Fig. 7A and a sample spiked with 94 ppb epichlorohydrin, Fig. 7B.

In order to improve the baseline resolution between epichlorohydrin and the solvent peak, a higher capacity column, IonPac AS11-HC, was used. Due to the higher ion-exchange capacity, the flow-rate was set at 1.5 ml/min and the following gradient was imposed: $t=0$ to 7 min, 2.5 m*M* KOH, from 7 to 20 min, KOH concentration was increased linearly to 40 m*M*. Results are shown in Fig. 7C) for the blank and in Fig. 7D for 94 ppb epichlorohydrin. As can be seen, in this column a better resolution can be obtained for epichlorohydrin that now elutes far from the void volume. Due to the blank signal, the detection limit for epichlorohydrin determination, evaluated as three times the background noise signal, has been calculated after subtraction of the blank peak. The value found is 70 ppt.

4. Conclusions

In this work we have developed an analytical method for epichlorohydrin determination by liquid chromatography. The method uses a derivatization reaction in order to transform epichlorohydrin to a hydroxypropanesulfonic acid which is easily determined by suppressed anion-exchange chromatography. Derivatization conditions have been optimized

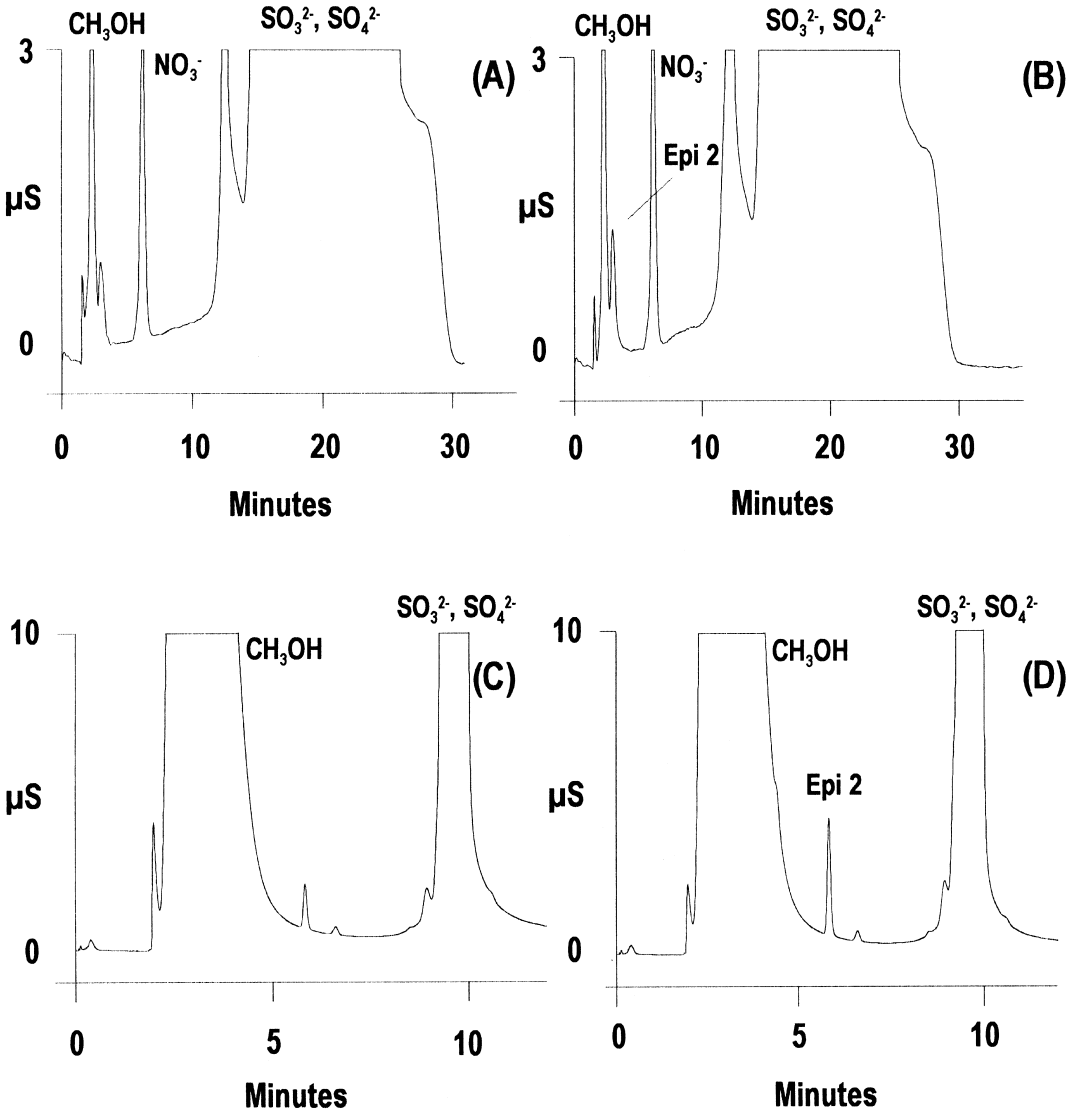

Fig. 7. Analysis of drinking water as such (A) and spiked with 94 ppb epichlorohydrin (B) with the method developed. Column: IonPac AS11. Eluent 2.5 m*M* NaOH. Flow-rate: 1 ml/min. Analysis of drinking water as such (C) and spiked with 94 ppb epichlorohydrin (D). Column: IonPac AS11-HC. Eluent: $t=0$ to 7 min, 2.5 m*M* KOH, from 7 to 20 min, KOH concentration was increased to 40 m*M*. Flow-rate: 1.5 ml/min. Preconcentration conditions as in Fig. 6, reaction conditions as in Fig. 5.

in order to obtain the highest yield of reaction. Eluent conditions as well as stationary phase have been optimized in order to achieve the best separation conditions. A preconcentration procedure has also been optimized for epichlorohydrin enrichment. The method developed, characterized by good detection limits and reproducibility, has been applied to epichlorohydrin determination in drinking water.

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