A Convenient Method for Epichlorohydrin Determination in Water Using Headspace–Solid-Phase Microextraction and Gas Chromatography

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Abstract

A simple procedure for epychlorohydrin determination in water is presented. In order to optimize the epichlorohydrin extraction conditions in water using headspace (HS)–solid-phase microextraction (SPME), followed by gas chromatography, an experimental design in two steps is performed. Firstly, a 2^{5-2} fractional factorial design for screening the significant variables is used. Secondly, a central composite design for optimizing them is carried out. The best experimental conditions are the followings: poly(dimethysiloxane)–divinylbenzene coating fiber; 20 min extraction time; 5°C extraction temperature; 300 g/L sodium chloride; and 20 mL HS volume in a 40-mL vial. Using the previous extraction conditions with gas chromatography (GC)–flame ionization detection equipment, a limit of detection (LOD) of 1.8 µg/L and a relative standard deviation (RSD) of 3.8% (for 25 µg/L) are obtained. With a GC electron capture detection equipment the RSD is 6.6% (for 5 µg/L), and the LOD found is lower (0.08 µg/L). The method is applied to the analysis of water from four treatment plants at the entrance and effluent stream. The standard addition method is used to quantitate the epichlorohydrin that is found in the raw water of the three wastewater treatment plants.

Introduction

Epichlorohydrin (1-chloro-2,3-epoxypropane) is an organic, colorless liquid that is used in the manufacture of glycerol, plastics, and other polymers, some of which are used in water-supplied systems as flocculating agents. The major toxic effects of epichlorohydrin are local irritation and damage to the central nervous system. The International Agency for Research on Cancer has placed it in group 2A (probably carcinogenic to humans) (1). The maximum contaminant level goal, based solely on possible health risk, has been set at zero by the Environmental Protection Agency (2). A value of 0.1 µg/L has been fixed in the European Council Directive for the waters intended for human consumption (3).

Although there are options based on ion chromatography after derivatization (4,5), the analytical methods to determinate epichlorohydrin mostly use gas chromatography (GC) with either electron capture detection (ECD) or mass spectrometric detection. Previously, an enrichment step is carried out such as liquid–liquid extraction (6), solid-phase extraction (SPE) (7), or purge and trap (8,9). Solid-phase microextraction (SPME) is a useful alternative for extraction because this technique does not require solvents and can be carried out directly from the liquid phase or from the headspace (HS) over the liquid samples. The direct immersion is used to determine volatile organic compounds, including epichlorohydrin (10). However, the extraction sampling in HS mode is more advisable when the matrix could affect the determination of the target compound, and a reduction in the extraction time is required (11). Hence, the HS extraction mode was the option for this study.

There are several variables affecting the HS–SPME procedure, such as fiber type, temperature, extraction time, salt addition, pH, desorption conditions, and HS volume. The classical method of optimization, considering one variable at a time, is difficult and time consuming. An experimental design that takes into account several variables simultaneously seems to be the most appropriate way to optimize the experimental conditions (12). This kind of approach, using SPME, has been applied for the determination of plastic monomers (13) and alkyl ethers as well as benzene, toluene, ethylbenzene, and xylene isomers (BTEX) (14) in water. The experimental design was applied for immersion conditions (13) and for optimizing the conditions working in HS–SPME extraction mode (14).

The aim of this study was to develop a method for epichlorohydrine determination in water using HS–SPME. The experimental design was planned in an attempt to find the best experimental conditions for HS–SPME. In order to extend the procedure, common GC equipment, equipped with flame ionization detector (FID) and ECD, was used following the HS–SPME extraction technique. Finally, the procedure was applied to the analysis of water from several treatment plants.

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Experimental

Reagents and materials

SPME holders and fibers [100-µm thickness poly(dimethylsiloxane) (PDMS) and 65-µm thickness PDMS–divinylbenzene (DVB)], sample vials (40 mL, amber glass), and PTFE-silicone septa were obtained from Supelco (Bellefonte, PA). The fibers were conditioned in the GC injection port according to the specifications provided by the supplier.

(±) Epichlorohydrin (99.5%) and (+) epichlorohydrin (≥ 98.5%) were purchased from Fluka (Buchs, Switzerland). Sodium chloride (99.5%) was supplied by Merck (Damstadt, Germany). Methanol (> 99.8 %) was from Panreac (Panreac Química S.A., Barcelona, Spain). The standard solution of 1000 mg/L epichlorohydrin was prepared in methanol, stored at 4°C, and used within 4 weeks. Working aqueous solutions, prepared just before use, were made from the stock methanolic solutions by spiking and mixing them with 20 mL organic free mineral water.

Care was taken to avoid airborne contamination by keeping vials capped and covering flasks and vials with cleaned aluminum foil. All the glassware and vials used for sampling and experiments were carefully washed with distilled water, filled and maintained overnight with 10% nitric acid, rinsed with acetone, and thermostated at 250°C for 2 h before using.

Apparatus and conditions

A HP 6890N GC equipped with two split–splitless injectors, FID, and µECD (Agilent Technologies, Wilmington, DE) was used. The injection port was fitted in the splitless mode, with the split–splitless purge valve opened 1 min after injection. The injection port temperature was 200°C, and helium served as carrier gas with a flow rate of 2.1 mL/min. GC–FID separation was accomplished with an Equity-5 column (30 m × 0.25-mm i.d., 0.25 µm of 5% diphenyl 95% dimethyl polysiloxane) from Supelco. The temperature program used was: 50°C for 1 min, increased 20°C/min to 170°C, and then 200°C for 2 min. The detector temperature was set to 280°C. GC–ECD chromatographic separation was accomplished with a capillary column DB-XLB (30 m × 0.32-mm i.d., 0.5 µm) from Agilent (Palo Alto, CA). For this equipment, the temperature program was the same as the previous one. The detector conditions were Ni^{63} ECD with nitrogen at 20 mL/min as the make up gas working at 250°C. A PC interfaced to the GC using Chemstation software (Agilent Technologies) was used for data acquisition and processing.

A Heidolph MR 3003 magnetic stirrer (Heidolph Elektro GmbH & Co KG, Kelheim, Germany) was used. PTFE-coated stir bars of 25 mm were put in the 40-mL amber vials just before runs. A cooling thermostat LAUDA RE 104 (Lauda Dr. R. Wobser, GmbH & Co.KG, Lauda-Königshofen, Germany) controlled the temperature. A titration vessel with thermostatic jacket was connected to the thermostat, and the sample vial was put inside of the vessel.

The experimental designs were performed, and the results were evaluated using the Statistica software package (Statsoft, Tulsa, OK).

Water samples

The samples were taken from four water treatment plants, one drinking water treatment plant and three wastewater treatment plants. In each plant, two samples were collected: at the influent entrance (1) and at the effluent stream (2). The sampling was done in June and in July 2005. The water samples were put in 100-mL glass containers that were completely filled, covered with aluminum foil, closed with a metallic cap, and transported to the laboratory in a cooler with ice. All the samples maintained in the cooler were analyzed within 24 h of the sampling. In order to check a potential contamination, a trip blank was included in addition to collected water samples.

HS–SPME procedure

Before extraction, 20 mL of the aqueous standards, water samples, or water samples plus appropriate standards for quantitation were put into 40-mL vials. In each vial, 6 g of sodium chloride was added (according to 300 g/L ratio) and one PTFE stir bar. After salt solution, the vial was put into the vessel connected to the thermostat at 5°C and maintained there 5 min until 5°C. Sample extraction was performed in HS mode, exposing the 65-µm PDMS–DVB fiber over stirred samples (1000 rpm). The extraction conditions were 5°C for the temperature and 20 min for the time. After sampling, the fiber was withdrawn into the needle of the holder, immediately placed in the GC

Table I. Experimental Variables, Levels, 2^{5-2} Fractional Factorial Design Matrix and Results (in Peak-Area Units) for Epichlorohydrin Determination with HS–SPME

Variable	Coded	Low level	High level
Fiber type	Fiber	PDMS (1)	PDMS-DVB (2)
Extraction time (min)	Time	2	15
Extraction temperature (°C)	Temp.	10	40
HS volume (mL)	HS-Vol	10	30
NaCl-salt concentration (g/L)	NaCl	0	300

Run	Fiber	Time	Temp	HS vol.	NaCl	Peak area
1	1	2	10	30	300	n.d.†
2	2	2	10	10	0	20.2
3	1	15	10	10	300	n.d.
4	2	15	10	30	0	54.6
5	1	2	40	30	0	n.d.
6	2	2	40	10	300	74.3
7	1	15	40	10	0	n.d.
8	2	15	40	30	300	65.9
9-C*	1	8.5	25	20	150	n.d.
10-C	2	8.5	25	20	150	72.8
11-C	1	8.5	25	20	150	n.d.
12-C	2	8.5	25	20	150	72.6

* C = Central point.
† Not detectable.

injector, and thermally desorbed for 1 min. No carryover was observed after this desortion time.

Blanks were periodically run during the analysis to verify the absence of contaminants. Three standards present in the water samples with concentrations close to epichlorohydrin were used for quantitation. The standard concentrations were from 5 to 40 µg/L.

Results and Discussion

In order to develop an adequate method using HS–SPME for epichlorohydrin determination in water, it is necessary to consider and optimize several parameters that affect the extraction procedure. An experimental design with two steps (screening and optimization) was used, searching for the best experimental conditions. In all the runs, 500 µg/L of (±) epichlorohydrin were added to the mineral water, and GC–FID was the equipment used. The (±) epichlorohydrin showed two peaks with retention times of 2.28 and 2.48 min. Because the latter gave the highest response, it was only considered in the evaluation of the experimental design. This second peak belongs to (+) epichlorohydrin, which was checked with the standard solution of this enantiomer.

Screening design

Screening is the first step in the efficient assessment of the factors involved in the studied analytical system. If a large number of factors were involved, reduced factorial designs such as fractional factorial designs were applied. Those designs were very useful because it was possible to detect the most significant variables with a few experiments.

On the basis of the literature and experience of the laboratory (10,11,13,14), five variables were selected to define the experimental field (one qualitative or categorical, and the other four quantitative or continuous). Type of fiber, extraction temperature, extraction time, HS volume, and sodium chloride concentration were the variables considered. In order to contrast the coating phases, the PDMS and PDMS–DVB fibers were chosen. The extraction time was from 2 to 15 min, and the extraction temperature was from 10°C to 40°C. The HS volume varied from 10 (¼ of the total volume of 40 mL vial) to 30 mL (¾ of the total volume of 40 mL vial). The concentration of NaCl salt ranged from 0 to 300 g/L. The addition of salt increases the ionic strength of the solution and decreases the solubility of compounds in water, therefore, improving the affinity to the fiber and increasing the extraction efficiency. The variables, codes, and low and high levels considered are shown in Table I.

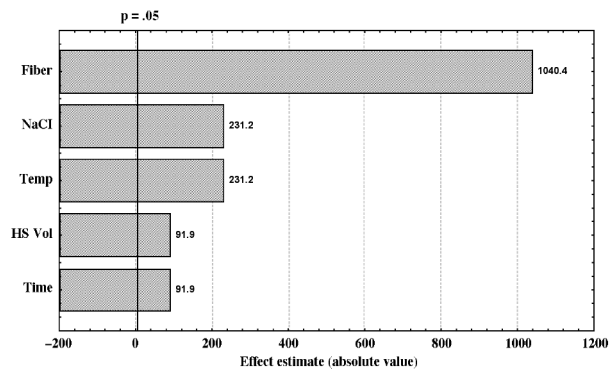

Figure 1. Pareto chart of the main effects obtained from 2^{5-2} fractional factorial design for epichlorohydrin determination.

A 2^{5-2} fractional factorial design was applied to evaluate the main effects. In total, the design matrix had 12 runs (four central points included). The design matrix and the response for the studied analyte (peak area in arbitrary units) are also given in Table I.

The data obtained was evaluated by analysis of variance test (not included), and the main effects were visualized using a Pareto chart (Figure 1). In the chart, the bar lengths are proportional to the absolute value of the estimated main effects. The chart also includes a vertical line corresponding to the 95% confidence interval. An effect, which exceeds this reference line, may be considered significant with regard to the response. The sign of the effect showed whether or not the response would be improved by passing a given factor from the lowest to the highest level. In this study, all the variables were significant. The fiber type was the most important variable,

Table II. Experimental Variables, Levels, CCD Matrix, and Results (in Peak-Area Units) for Epichlorohydrin Determination with HS–SPME

Variable	Coded	Low level	Medium level	High level
Extraction temperature (°C)	Temp.	15	30	45
Extraction time (min)	Time	5	10	15
NaCl concentration (g/L)	NaCl	55	135	215

Run	Temp	Time	NaCl	Peak area
5	45	5	55	26
8	45	15	215	37
16-C*	30	10	135	55
6	45	5	215	48
14	30	10	269	91
13	30	10	0	27
12	30	18.4	135	48
3	15	15	55	57
1	15	5	55	40
9	4.7	10	135	67
15-C	30	10	135	53
11	30	1.6	135	41
7	45	15	55	19
18-C	30	10	135	56
4	15	15	215	103
17-C	30	10	135	56
2	15	5	215	77
10	55	10	135	19

* C = Central point.

with a positive effect for the PDMS–DVB coating. The next most influential factors in the response were the salt concentration and the extraction temperature. Hence, the chosen fiber was the one with the highest response (i.e., PDMS–DVB). Taking into account the slight differences in response and the practical handling, an intermediate HS volume of 20 mL was chosen for the following optimization step. The PDMS–DVB mixed-coating fiber and ½ HS volume ratio (20 mL HS volume/40 mL total vial volume) were also the chosen conditions for the variables in the simultaneous dialkyl ethers and BTEX determination in water (14).

Optimization design

The second step was to optimize the significant variables obtained with the fractional factorial design using a central composite design (CCD). The three considered variables and their low, central, and high levels were the followings: NaCl concentration (NaCl, 55, 135, and 215 g/L), extraction temperature (15°C, 30°C, and 45ºC), and extraction time (5, 10, and 15 min). Those values are included in Table II.

CCD consisted of the points of factorial design (2^N) increased with ($2N + 1$) star points (N being the number of variables). In this work, 2^3 increased with ($2 \times 3 + 1$) star points. The star points were located at $+\alpha$ and $-\alpha$ from the center of the experimental domain. An axial distance (α) was selected with a value of 1.6818 in order to establish the rotatability condition that generates information equally in all directions. The runs at the center of the experimental field were performed three times more. Therefore, in total, the matrix of the CCD design consisted of 18 experimental runs. The runs were randomly carried out, and each run was done twice with two independent samples. The average values of the two data (in arbitrary units of peak area) are shown in Table II.

The next step was to find the conditions of the independent variables (extraction temperature, extraction time, and NaCl concentration) that maximize the response of the dependent variable (epichlorohydrin peak area). In Statistica for standard CCD, a second-degree polynomial model is used. The regression coefficients obtained were used in computing predicted values for the dependent variable at different combinations of the independent variables levels. Also, there is an option for predicting values of the dependent variable based on user-defined factor values.

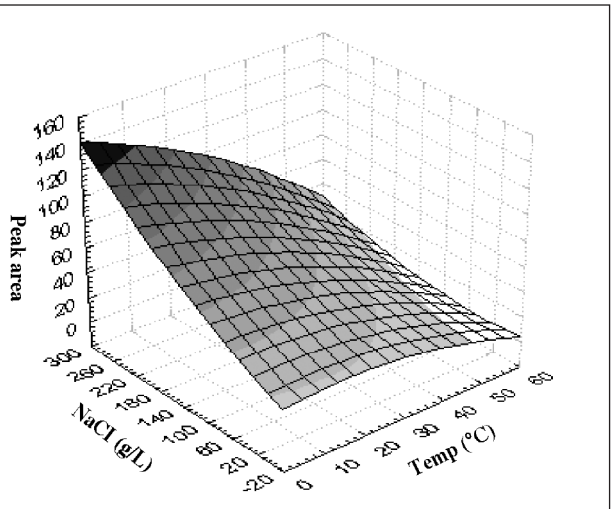

Figure 2. Response surface for peak area from the central composite design considering extraction temperature versus NaCl concentration.

The shape of the fitted response can best be visualized in graphs such as 3-dimensional (3-D) plots. The result for the CCD experiment involving the response (peak area) as a function of the temperature and the NaCl concentration is shown in Figure 2. As can be seen, the highest responses were reached when the extraction temperature was close to 5°C and the NaCl concentration was around 300 g/L. A similar 3-D plot was obtained for extraction time and NaCl concentration, which allowed us to deduce the favorable extraction time of 20 min.

Taking into account the results, the working extraction conditions to obtain the best response were: PDMS–DVB fiber; HS 20 mL (in 40-mL vial); 5°C for extraction temperature; 20 min for extraction time; and 300 g/L of NaCl concentration.

Analytical characteristics

Using the best extraction conditions, the linearity of the HS–SPME method for epichlorohydrin determination in water was evaluated. The experiments were run with both GC–FID and GC–ECD equipment. The latter was considered because epi-

Table III. Studied Linear Ranges, Correlation Coefficients, LOD, and Repeatability (%RSD) of the Optimized HS–SPME Procedure for Epichlorohydrin Determination in Water

				Repeatability		
GC detector	Range (µg/L)	r^2	LOD (µg/L)	Concentration (µg/L)	n	RSD (%)
FID (t_R* = 2.28 min)	5–50	0.9822	14.3	25	5	1.3
FID (t_R = 2.48 min)	5–50	0.9967	1.8	25	7	3.8
ECD (t_R = 4.43 min)	0.1–10	0.9978	0.08	5	7	6.6
ECD (t_R = 4.52 min)	0.25–25	0.9972	0.38	5	7	5.8

* Retention time.

Table IV. Epichlorohydrin Concentration (µg/L) in Water Samples from Water Treatment Plants

Treatment plants	Influent	Effluent
Drinking water A	n.d.	n.d.
Wastewater B	14	21
Wastewater C	9	9
Wastewater D	19	0.3

chlorohydrin is an organochloride compound, which could improve the signal and get a lower limit of detection (LOD). With this GC–ECD equipment, the (±) epichlorohydrin also gave two peaks at 4.43 and 4.52 min retention time. The first peak was assigned to (+) epichlorohydrin after checking with the pure (+) enantiomer.

The calibration standard samples were prepared in two ranges, 5–50 µg/L for GC–FID and 0.1–25 µg/L for GC–ECD. The HS–SPME procedure showed a good linear behavior with correlation coefficients (r^2) higher that 0.997 for GC–ECD and 0.996 for GC–FID (signal at 2.48 retention time). The procedure repeatability, expressed as relative standard deviation (RSD in %), was obtained from the results of five or seven consecutive and independent samples being analyzed on the same day. The concentrations used in the repeatability runs were 25 µg/L for GC–FID and 5 µg/L for GC–ECD. The RSD-obtained values were less than 7%. All those data are included in Table III.

The LODs were calculated considering that the signal differed three times from the standard deviation of the blank signal. The LOD using GC–FID was of the µg/L order, obtaining the lowest value at 2.48 min retention time (1.8 µg/L). This value is similar to 1.2 µg/L obtained working with SPME in immersion mode and PDMS coating fiber (10). In the latter work, the LOD was calculated considering signal-to-noise ratio (s/n = 3). The LOD found with the proposed method, GC–ECD, was lower, and considering the signal at 4.43 min, the value 0.08 µg/L was enough to distinguish it from the restricted level of drinking water (0.1 µg/L). This LOD was better than the value obtained working with static HS (9), equivalent to the level found using SPE for enrichment (7) and slightly higher than the value found using purge and trap prior to chromatographic detection (9). In all these works, the determination was done by GC–ECD.

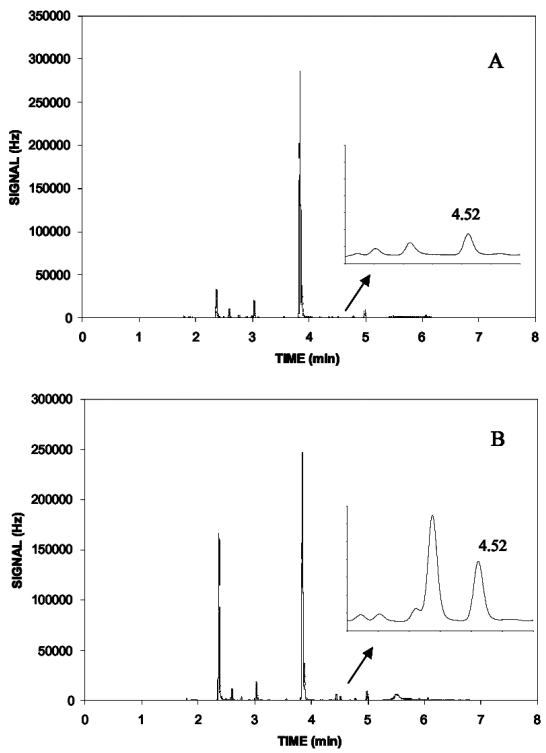

Figure 3. GC–ECD chromatograms of the effluent sample from wastewater treatment plant-C (A) and with 40 µg/L of (±) epichlorohydrin standard (B).

Water samples application

The proposed HS–SPME method was applied for the determination of epichlorohydrin in water samples from influent and effluent of water treatment plants. The GC–ECD equipment was used in order to detect epichlorohydrin at as low levels as possible

The results are showed in Table IV. The epichlorohydrin was not detected in the drinking water plant. However, the analyte was found in the urban wastewater before the entrance in the B, C, and D treatment plants. In these plants, the levels that appear in the effluents should be related to wastewater influent and not to the treatment with flocculant agents mostly based in polyacrylamide polymers. In plant D the treatment was more efficient than in the others plants, and the level of epichlorohydrin was remarkably reduced in the effluent. One interesting fact was that the only peak found was the second one (at 4.52 min retention time). As an example, the Figure 3 shows the chromatograms of the effluent point from the wastewater treatment plant C. The first one belong to the original sample (A) and the second one (B) to the sample plus 40 µg/L of (±) epichlorohydrin standard.

Conclusion

A useful method for epichlorohydrin determination in water using HS–SPME was developed. The utility of the experimental design was also shown in the screening and optimization of the extraction conditions for HS–SPME in a reasonable number of runs.

The main advantage of the method was based on the simplicity of the equipment. A PDMS–DVB fiber for the extraction, a water bath for temperature control, and a GC with FID and ECD detectors were required. Using GC–FID allows for determining samples with concentrations higher than 2 µg/L. Samples with low levels could be analyzed by means of more sensitive detectors such as ECD. In this case, the LOD obtained was slightly lower than the 0.1 µg/L regulated level for drinking water by the European Community.

The applicability of the method with real and more complex matrices was tested with the analysis of several samples from drinking and waste water treatment plants.

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