Analysis of acrylamide in drinking water by SPE and GC–MS

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Received: 23 October 2018 / Accepted: 4 March 2019 / Published online: 15 March 2019 © The Author(s) 2019

Abstract
The present study aimed to evaluate the levels of acrylamide in drinking water by solid phase extraction (SPE). After SPE, water extracts were analyzed using gas chromatography–mass spectrometry (GC–MS) system. Thirty drinking water samples were analyzed in the study. Acrylamide was detected in 12 samples. The levels of acrylamide in drinking water samples were less than 85 ng l⁻¹. The limit of detection and limit of quantification were 4 and 13.20 ng l⁻¹, respectively.

Keywords Drinking water · Acrylamide · SPE · GC–MS

Introduction
Acrylamide (C₃H₅NO, prop-2-enamide, \( M_w \); 71.08 g mol⁻¹) is a small chemical compound used for over 50 years; now that is used mainly for the monomer to synthesize polyacrylamides and its copolymers (EHC 49 1985). Acrylamide is used as flocculants to purify drinking water and wastewater (Friedman 2003).

It is used in many several industrial sectors such as paper, plastics, textile, dyes and cosmetics (Alpmann and Morlock 2008). The high water solubility of acrylamide causes acrylamide to be present in drinking water. Acrylamide is one of the chemical structures of the carcinogen group (IARC 1994, 1997). The World Health Organization (WHO) has stated that the guideline set value associated with the maximum concentration of acrylamide in drinking water is 0.5 µg l⁻¹ (WHO 1991, 1993, 2011). Also, restrictive quality requirement limits of 0.1 µg l⁻¹ for water intended for human consumption have been regulated in European Union and take part in the EU 98/83/EC Drinking Water Directive (Council Directive 98/83/EC 1998). Animal studies have shown that acrylamide has a negative effect on health (Johnson et al. 1986; Neumann 1991; Alison et al. 1994; Friedman et al. 1995; Ben-Jonathan et al. 2008; Beland et al. 2013).

To date, several analytic methods for the analysis of acrylamide in water have typically involved chromatographic (liquid chromatography, gas chromatography) separation followed by spectrophotometric detector [ultraviolet (UV) detector, diode array detector (DAD), fluorescence detector], electron capture detector (ECD) or mass spectrometry (Cavalli et al. 2004; Güven and Gezgin 2005; Alpmann and Morlock 2008; Kepekci et al. 2012; Yamini et al. 2012; Lim and Shin 2013; Backe et al. 2014; Sobhi et al. 2017). Most analysis of acrylamide achieved in experiments to date has been based on derivatization or without derivatization (Cavalli et al. 2004; Güven and Gezgin 2005; Alpmann and Morlock 2008). The extraction of acrylamide from water samples is usually achieved via hollow fiber liquid phase microextraction (Sobhi et al. 2017), liquid–liquid extraction (Güven and Gezgin 2005; Backe et al. 2014) and solid phase extraction (Alpmann and Morlock 2008).

The aim of the study is to make acrylamide analysis in 30 drinking water samples using SPE method by GC–MS without the derivation step.

Materials and methods

Chemicals, reagents and material

Methanol, acrylamide and acetone were obtained from Merck and Sigma-Aldrich. Restek™ CarboPrep Cartridges were used for solid phase extraction.
Drinking water samples

Drinking water samples were taken from different provinces in Burdur and Isparta. Bottled water samples of different brands were purchased from local markets in Burdur. In this study, a total of 30 water samples were analyzed.

SPE cleanup procedure

Restek™ CarboPrep cartridges (6 ml, 500 mg) were placed in the manifold system and activated with 2 ml acetone and finally rinsing 2 ml 0.1% formic acid. The water sample (about 250 ml) was loaded on the column and the sorbents were dried. Acrylamide was eluted from the cartridges using 2 ml acetone (Acrylamide analysis by gas Chromatography 2004).

Chromatography and apparatus

An Agilent 7890A GC equipped with a 5975 MS detector, a 7693B automatic sampler and a MSDCHEM (Agilent, USA) data system was used for the determination of acrylamide in the analyzed water samples. GC temperature program and operating conditions are given in Table 1 (Agilent Technologies Inc 2014).

Results and discussion

Method parameters

Stock standard solution of acrylamide was prepared in acetone. Six different concentrations are used for calibration curves. Linear regression analysis was carried out by plotting peak area (y) versus acrylamide concentration (x). A signal-to-noise (S/N) ratio of 3:1 is generally considered suitable ratio for the LOD. A typical S/N ratio is 10:1 for a LOQ. The extraction recovery was determined by spiking samples with acrylamide in three replicates; they were extracted as previously described. The LOD and LOQ were calculated to be 4.00 and 13.20 ng l⁻¹, respectively.

Table 1  Temperature program and operating condition
\[
\begin{array}{|c|c|c|c|}
\hline
\text{Start (°C)} & \text{End (°C)} & \text{Rate (°C/min)} & \text{Hold time (min)} \\
\hline
60 & 60 & – & 1 \\
60 & 240 & 20 & 20 \\
\hline
\end{array}
\]

Operating condition

- Injection port temperature: 240 °C
- Detector temperature: 240 °C
- Ion source temperature: 230 °C
- Carrier gas: He
- Flow rate: 15 psi

This value was adequate for the monitoring of acrylamide at the limit value of 0.5 µg l⁻¹ as demanded by WHO and EPA and 0.1 µg l⁻¹ in drinking water as stipulated by EU. In different studies, LOD values have been reported between 1–200 ng l⁻¹ (Cavalli et al. 2004; Lim and Shin 2013; Kepekci et al. 2012; Backe et al. 2014; Yamini et al. 2012; Sobhi et al. 2017; Alpmann and Morlock 2008). The LOD and recovery values obtained in this study are similar to those in the literature. Precision is a measure of the degree of reproducibility/reproducibility of the analytical method tested under the working conditions. Repeatability was measured using three different concentrations of acrylamide prepared and analyzed. Intraday and interday instrument variations were examined to determine the sensitivity of the proposed analytical methods (Table 2). RSD values obtained from intraday and interday studies are lower than 5%.

The accuracy of the analytical method being tested is expressed as the proximity of the measured value to the actual value for the sample. In our study, acrylamide was added to the water sample (Table 3). For the accuracy studies, the sample preparation was carried out exactly. Accuracy is generally expressed as the standard deviation or percent relative error and the average mean recovery % of the analytical method (Table 4).

Table 2  Method parameters
\[
\begin{array}{|c|c|}
\hline
\text{Parameter} & \text{Equation/value} \\
\hline
\gamma & 159.971.29x + 246.17 \\
R^2 & 0.9998 \\
\text{Limit of detection (ng l}^{-1}) & 4.00 \\
\text{Limit of quantification (ng l}^{-1}) & 13.20 \\
\hline
\end{array}
\]

Analytical results

The content of acrylamide in various drinking water samples was investigated in Table 5.

The level of acrylamide in drinking water samples ranged from 14.53 to 85.00 ng l⁻¹. The concentrations of acrylamide detected at the drinking water studied currently were well below the 0.1 µg l⁻¹ and 0.5 µg l⁻¹ limits required by the EU and EPA. Igisu et al. (1975) reported that mean
Acrylamide concentration was 400 mg l⁻¹. Brown and Rhead (1979) have reported the acrylamide level in sea water was 3.4 µg l⁻¹.

### Table 3  Precision data in this study

| S. no. | Intraday for instrument | Interday for instrument |
|--------|-------------------------|-------------------------|
|        | Amount of acrylamide taken (µg l⁻¹) | Amount of acrylamide found (µg l⁻¹) | Mean concentration | RSD (%) | Amount of acrylamide taken (µg l⁻¹) | Amount of acrylamide found (µg l⁻¹) | Mean concentration | RSD (%) |
| 1      | 1.50                    | 1.55                    | 1.49                | 3.45     | 1.50                    | 1.47                    | 1.47               | 2.45    |
| 2      | 3.00                    | 3.09                    | 3.10                | 2.75     | 3.00                    | 2.95                    | 2.98               | 3.67    |
| 3      | 5.00                    | 4.98                    | 4.95                | 1.70     | 5.00                    | 4.88                    | 4.94               | 1.88    |

### Table 4  Accuracy/Recovery studies

| S. no. | Amount of acrylamide added (µg l⁻¹) | Amount of acrylamide found (µg l⁻¹) | % Recovery | Average recovery (%) | RSD (%) |
|--------|-----------------------------------|-----------------------------------|------------|----------------------|---------|
| 1      | 2.00                              | 1.75                              | 87.50      | 86.83                | 1.85    |
| 2      | 4.00                              | 3.50                              | 87.50      | 89.00                | 1.84    |
| 3      | 6.00                              | 5.53                              | 88.83      | 89.28                | 0.57    |

### Table 5  Acrylamide content in drinking water

| Drinking water | Acrylamide content (ng l⁻¹) [mean ± confidence interval (95%)] |
|----------------|---------------------------------------------------------------|
| 1              | 85.00 ± 6.55                                                  |
| 2              | 48.33 ± 3.17                                                  |
| 3              | 61.00 ± 4.34                                                  |
| 4              | 65.00 ± 7.69                                                  |
| 5              | 27.33 ± 9.22                                                  |
| 6              | 42.00 ± 6.31                                                  |
| 7              | 14.53 ± 7.34                                                  |
| 8              | 56.00 ± 9.45                                                  |
| 9              | 42.00 ± 6.31                                                  |
| 10             | 22.06 ± 7.22                                                  |
| 11             | 18.15 ± 8.74                                                  |
| 12             | 16.06 ± 9.85                                                  |

### Conclusions

This study was done without derivatization. The level of acrylamide in drinking water samples analyzed in this study. The LOD was calculated to be 4.00. This value was adequate for the monitoring of acrylamide at the limit value of 0.5 µg l⁻¹ as demanded by WHO and EPA and µg l⁻¹ in drinking water as stipulated by EU. Acrylamide was detected in 12 samples. The amount of acrylamide in the samples outside the table was below the detection limit. Thirty drinking water samples were analyzed in the study. Acrylamide was detected in 12 samples.

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