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The determination of acrylamide in environmental and drinking waters by large-volume injection – hydrophilic-interaction liquid chromatography and tandem mass spectrometry

Will J. Backe[a,*], Virginia Yingling[b], Todd Johnson[c]

[a] Public Health Laboratory Division , Minnesota Department of Health, 601 Robert Street North, P.O. Box 64899, Saint Paul, MN 55164-0899, USA
[b] Environmental Health Division, Minnesota Department of Health, 625 Robert Street North, P.O. Box 64975, Saint Paul, MN 55164-0975, USA
[c] Environmental Health Division, Minnesota Department of Health, 705 5th Street NW, Bemidji, MN 56601-2933, USA

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ABSTRACT

A simple and sensitive analytical method was developed to quantify levels of acrylamide in environmental and drinking waters. The analytical method consisted of solvent exchanging acrylamide from 2 mL of water into 2 mL of dichloromethane using acetonitrile as an intermediate. The sample was then directly analyzed by large-volume (750 μL) injection – hydrophilic-interaction liquid chromatography and tandem mass spectrometry. The method detection limit and reporting level were 2.4 ng/L and 17 ng/L of acrylamide, respectively. The recovery of acrylamide during solvent exchange was 95 ± 2.8% and the matrix effects were 12 ± 2.2% in river water. The use of atmospheric-pressure chemical ionization reduced matrix effects; however, it also reduced method sensitivity by a factor of 2.2 compared to electrospray ionization. Matrix effects were compensated for by the use of an isotopically-labeled internal standard and the method accuracy was 89 ± 3.0% at 25 ng/L of acrylamide and 102 ± 2.6% at 250 ng/L of acrylamide. The precision of the method was less than 6% relative standard deviation at both 25 ng/L and 250 ng/L of acrylamide. Samples from a sand-and-gravel mine and a drinking-water treatment plant were acquired to demonstrate the method. The concentrations of acrylamide at the sand-and-gravel mine were up to 280 ng/L. In the drinking-water treatment plant, the concentration of acrylamide was approximately double in the finished drinking water when compared to other stages in the drinking-water treatment process. Disinfection or fluoridation may result in higher concentrations of acrylamide in finished drinking water; however, further research in this area is necessary.

1. Introduction

Acrylamide (AA) is a small (MW = 71 g/mol) water soluble (215 g/100 mL at 30 °C) [1] molecule that is used mainly for the production of polyacrylamide and its copolymers [2]. In turn, polyacrylamide is used as a flocculent in wastewater treatment, drinking water treatment, and ore and sand mining [3,4]. Acrylamide is present as an impurity in polyacrylamide at concentrations as high as 5% [2]. While research suggests that under most environmental conditions polyacrylamide does not degrade to AA [5], it may do so to varying degrees in the presence of Fe^{3+} and sunlight [6], under UV irradiation [7,8], and at elevated temperatures [8,9]. Acrylamide also forms during the cooking (frying, baking, roasting, etc.) of foods through reactions between amino acids and reducing sugars [10]. The International Agency for Research on Cancer classified AA as a "probable carcinogen" to humans based on animal studies [11]. Furthermore, AA is neurotoxic in humans [12,13] and animals [14] and is a reproductive toxin in animals [15].

Most of the analytical methods for the detection and quantification of AA are targeted toward foods [10,16]. However, given the applications of polyacrylamide, analytical methods are needed to quantify concentrations of AA in environmental and drinking waters. To date, only a few methods exist for such purposes. Gas chromatographic (GC) methods for the determination of AA in water have used electron capture or mass spectrometric (MS) detection; however, these methods required AA derivatization and liquid–liquid extraction before analysis [17–19]. Kawata et al. [20] developed a GC–MS method for the quantification of AA and other polar molecules without derivatization. However, that method required the extraction of 500 mL of surface water on four SPE cartridges (C18, Activated Carbon Fiber × 3) coupled in series [20].

* Corresponding author. Tel.: +1 651 201 4864.
E-mail addresses: will.backe@state.mn.us, Will.Backe@Gmail.com (W.J. Backe).

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The use of high-performance liquid chromatography (HPLC) [21–25] for the analysis of AA is another way to avoid derivatization steps, which are often laborious and result in variable yields [18,19,26]. In the past, HPLC analyses of AA that employed UV-detection suffered from high detection limits (3–10 μg/L) [27,28]. More recently, tandem mass spectrometry is used with HPLC in environmental analyses due to its high selectivity and increased sensitivity. However, trace amounts of AA in water must still be concentrated before HPLC–MS/MS which is problematic because AA is poorly retained on many phases used for solid-phase extraction (SPE) [29]. A method by Chu et al. [25] circumvented the use of SPE by concentrating AA through coevaporation with water using a rotary evaporator at 90 °C under a vacuum. However, coevaporation was a low throughput method because only one sample could be processed per rotary evaporator and sample preparation took 90 min [25].

Large-volume injection (LVI) is a technique that avoids the need for extraction-based analyses [30,31]. During LVI-based analyses, a larger-than-traditional volume (e.g., 750 μL) of a sample is injected onto an HPLC column, and if the sample solvent is eluotropically weak, the analyte focuses (concentrates) at the head of the column [32]. Because minimal (e.g., centrifugation) or no sample preparation is typically involved, LVI eliminates analyte losses due to inefficient sample extractions [32]. However, when LVI was previously employed for the analysis of AA, the methods suffered from high detection limits (>100 ng/L AA)[23,24] unless specialized ionization technology not available for all mass spectrometers was used [23].

A drawback to current HPLC-based methods is that reverse-phase columns have a low retention capacity for AA [29]. In studies that report the use of C18 and IonPac ICE-AS1 (sulfonate functionalized poly[styrene-divinylbenzene]) columns for HPLC AA elutes right after the column void-volume (k = less than 1 [see supplementary material (SM)]) [21–25]. In contrast, hydrophilic-interaction liquid chromatography (HILIC) is designed specifically for the retention of small polar molecules [33]. During HILIC, a polar stationary phase is used with a mobile phase that is composed (typically) of greater than 70% organic solvent (usually acetonitrile) [34]. While HILIC is becoming increasingly used by analysts to separate small polar analytes [34], a method using HILIC has yet to be developed for the analysis of AA.

The objective of this research was to develop and validate a simple and sensitive large-volume injection method utilizing HILIC separation for the analysis of AA in drinking and environmental waters. To avoid sample extractions, water samples were directly solvent exchanged into dichloromethane using acetonitrile as an intermediate (Fig. 1). After the solvent exchange, the sample was injected directly onto a HILIC column which avoided any further sample preparation. The finalized method was demonstrated on water samples from a sand-and-gravel mine and a drinking-water treatment plant.

2. Materials and methods

2.1. Chemicals and materials

Standards of AA purchased from Sigma–Aldrich (St. Louis, Missouri) and Alfa Aesar (Ward Hill, Massachusetts) were greater than 99% purity. There was no difference in the quantification of AA in water samples when the two sources of AA were compared (see SM). $^{13}C_3$-Acrylamide ($^{13}C_3$-AA) (99% isotopically pure) was purchased from Sigma–Aldrich and used as an internal standard. LC–MS grade reagent water, UV grade acetonitrile, and HPLC grade dichloromethane were obtained from Burdick and Jackson® (Honeywell, Morristown, New Jersey) Formic acid of 99% purity was acquired from Acros Organics (Geel, Belgium). Nitrogen gas was generated from an in-house store of liquid nitrogen and was greater than 99.99% purity.

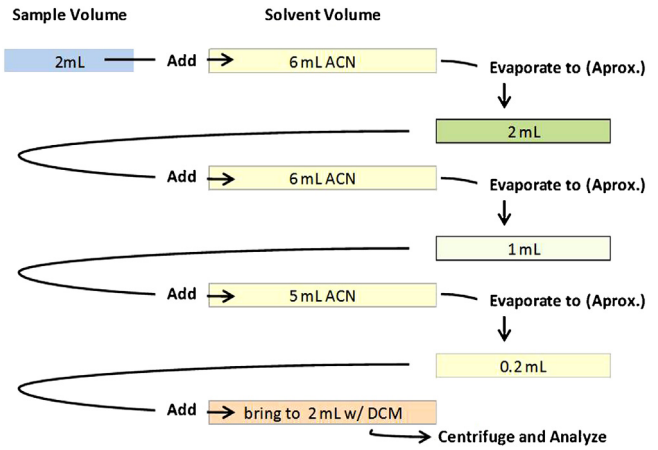

Fig. 1. An overview of the sample preparation process. ACN stands for acetonitrile and DCM stands for dichloromethane.

2.2. Sample collection

Water samples were collected in 125 mL high-density polyethylene (HDPE) bottles that were selectively prescreened and found to be free of AA background. After samples were collected, they were put on ice in a cooler until they reached a location where they could be frozen. Samples remained frozen until they were processed and all samples were processed in duplicate. Acrylamide concentrations in reagent water, tap water, and river water remained stable under storage conditions for 2 months (duration of the stability study) (see SM).

Water was sampled at four locations from a sand-and-gravel mine in Central Minnesota. Two grab samples were taken from the west and east ends of a 168 m long holding pond where water from a sand-and-gravel processing plant enters and exits, respectively. Flocculent is added at the west end of the holding pond to clarify the water for reuse. The water moves from the first holding pond to a second holding pond (also 168 m long) that was not sampled. A grab sample was taken from the processing plant where the water from the second settling pond is reused. A final water sample was taken from a tap connected to a drinking water well at the mine.

Four grab samples were taken from a drinking water treatment plant in Northern Minnesota. Water enters the drinking water treatment plant through a screened intake and is then pumped to a splitter box where flocculent is added. The splitter box directs the water to a clarification tank followed by a filtration tank where a gravity-fed anthracite and sand filter is used. After filtration, the water is disinfected using chloramination and treated with fluoride. Samples were taken from the following locations in the drinking water treatment plant: the splitter box, the clarification tank, immediately after the filtration tank, and from the finished drinking water.

A grab sample from the Mississippi River in Saint Paul, MN was collected in a 500 mL HDPE bottle and used for all method development and validation experiments.

2.3. Sample preparation

Samples were thawed and a 2 mL aliquot of each was transferred into a 15 mL polypropylene centrifuge tube containing 6 mL of acetonitrile and 200 pg of $^{13}C_3$-AA (internal standard). The sample was