

## CHAPTER I

### INTRODUCTION

Generally, natural water in the environment such as rivers, lakes and surface waters were frequently contaminated with pesticides, endocrine disrupting chemicals, surfactants, textile dyes, alga toxins, microorganisms, natural organic matters and inorganic pollutants [1-3]. Emergent contaminants are harmful for human especially microorganism pathogens, which provide waterborne diseases such as dysentery, typhoid and cholera [4,5]. Therefore, disinfectants have been utilized in water treatment process for human consumption to kill waterborne pathogens (e.g. *E. coli*, *V. cholerae*, *Coliform*) and prevent them from regrowth in the distribution systems.

In Thailand, chlorine has long been used as disinfectant for water supply prepared from the Chao Phraya River [6]. Despite of its effectiveness of waterborne disease prevention, chlorine can react with natural organic matters and/or inorganic substances in water to form a wide variety of disinfection by-products (DBPs) some of which are health hazards. Trihalomethanes (THMs) and haloacetic acids (HAAs) are two major groups of halogenated DBPs resulted from drinking water chlorination [7]. Several studies in epidemiology and toxicology have reported that existence of DBPs in drinking water increases risks of cancer and reproductive disorder [8-11]. For these reasons, the US Environmental Protection Agency (US EPA) [12], the European Union (EU) [13] and the World Health Organization (WHO) [14] have established maximum contaminant levels for THMs and HAAs in drinking water as shown in Table 1.1. In Thailand, the Metropolitan Waterworks Authority (MWA) has adopted the regulated values for THMs and HAAs according to the WHO guideline.

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**Table 1.1** Standard/guidelines related to DBPs in various jurisdictions of the world.

Analyte	US EPA regulation ( $\mu\text{g/L}$ ) [12]	EU standard ( $\mu\text{g/L}$ ) [13]	WHO guideline ( $\mu\text{g/L}$ ) [14]
Trichloromethane	-	-	200
Bromodichloromethane	-	-	60
Dibromochloromethane	-	-	100
Tribromomethane	-	-	100
Total trihalomethanes	80	100	$\sum_{i=1}^4 \frac{\text{THM}}{\text{WHO}} \leq 1$
Dichloroacetic acid	-	-	50
Trichloroacetic acid	-	-	100
Total haloacetic acids 5 <sup>a</sup>	60	-	-

<sup>a</sup> The sum of five HAAs, i.e. mono-, di-, and trichloroacetic acids and mono-, and dibromoacetic acids.

The development and application of sample preparation and analytical methods for the determination of THMs and HAAs in water have been reported in several literatures such as liquid-liquid extraction (LLE) [15-18], direct aqueous injection (DAI) [19,20], headspace (HS) [21-24], purge and trap (P&T) [25,26] and solid-phase microextraction (SPME) [27-32] followed by gas chromatographic separation with electron capture detector (ECD) or mass spectrometer detector (MSD). For the determination of HAAs that are low volatility and high polarity with carboxylic functional groups, derivatization prior to analysis is necessary [33].

In the view of the methods used for the extraction of THMs and HAAs in water, LLE has some practical disadvantages which require large amounts of toxic solvents; moreover, there is a problem of emulsion formation and it is time consuming procedures [34-36]. For direct aqueous injection, although the sample is directly injected into the GC column without any pretreatment, contamination of the injector and the GC column with sample matrix (non-volatile compounds, salts, etc.) and rapid deterioration of system performance are serious disadvantages [37,38]. Headspace is relatively poor precision and sensitivity compared to purge and trap [39,40]. Purge and trap requires special instrument, more time consuming technique and carry over may occur in the system [41,42]. For solid-phase microextraction, despite that it combines extraction and preconcentration into one step and includes analyte introduction to the GC by thermal desorption in single equipment, SPME fiber

coatings are limited, practically fragile, having a finite lifetime and relatively expensive; moreover, sample carry over is also a problem [43-45].

Recently, solvent microextraction involving the miniaturization of LLE into a microdrop known as single-drop microextraction (SDME) has been developed [46-49]. Although SDME has demonstrated a simple, inexpensive, fast, and virtually solvent free sample preparation technique, drop stability and low sensitivity is often problematic [50,51]. Subsequently, solvent microextraction based on liquid films known as liquid-phase microextraction (LPME) has been introduced using a single, low cost, disposable, porous hollow fiber membrane [52-54]. This technique, the organic solvent is impregnated and contained within the lumen of the porous hollow fiber as an interface between sample solution and extracting phase into where the analyte is extracted. LPME is simple, fast, inexpensive and environmental friendly sample preparation technique. In addition, LPME gives high enrichment factor and combines sample extraction, preconcentration and cleanup into a single step [55-57]. Therefore, development of LPME for determination of trace analytes in environment has become more interesting.

The objective of this study is to develop a simple, inexpensive and environmental friendly method for determination of THMs and HAAs in water using LPME and apply this technique for determination of these compounds in drinking waters and public waters.

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