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Analytical Methods for Determination of Regulated and Unregulated Disinfection By-Products in Drinking Water: A Review.

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Chlorine is a household name as a drinking water disinfectant. Incidentally, its application often results in the formation of toxic products generally called disinfection by-products (DBPs) some of which are halonitromethanes (HNMs), haloacetonitriles (HANs), trihalomethanes (THMs), halo acetic acids (HAAs). Similarly, the use of ozone, chloramine and chlorine dioxide for water treatment results in the formation of emerging unregulated DBPs) such as nitrosodimethylamine (NDMA), and other nitrogen -containing DBPs known to be more toxic than the regulated DBPs. Because DBPs are absolutely soluble in water, less stable and volatile at high temperature during analysis, no common method is available for the analysis of these chemicals. In view of this analytical challenge there is the need to review the existing methods. The aim of this study is to present a survey of the existing methods used for the analysis of DBPs in drinking water with a view to identifying their limitations and suggest the possible ways of method improvement. The review identifies environmental unfriendliness of the commonly used solvent methyl tert-butyl ether (MBTE), the fibre used in the dispersive liquid-liquid microextraction (DLLME) continues to be a source of impurity to the analyte. The analytical instrument with high sensitivity and robust library database is essential in the analysis and overall identification of DBPs.

Keywords: Disinfection by-products, water sample, preservative chemicals, analytical methods, solvent extraction.

1. Introduction

The accessibility to safe drinking water is a fundamental health right (Boorman et al., 1999; Richardson, et al., 2007). The use of disinfectants such as chlorine, ozone, chlorine dioxide, and chloramines as a standard treatment practice results into reduction in the mortality from water-borne diseases such as cholera, typhoid, and amoebic dysentery (Ohanian, 1989; Boorman et al., 1999; Ohanian, 1989; Richardson et al., 2007). More than 600 disinfection by-products (DBPs) have been reported in drinking water, arising from the use of disinfectants for water treatment (Bond et al., 2011; Krasner et al., 2006). However, underground water in the proximity of industrial effluents and anthropogenic activities generate precursors for the formation of DBPs (Mitch et al., 2003; Wang et al., 2015; Chen, 2018; Li et al., 2018; Liu, 2018).

Epidemiological studies have revealed that an exposure to chlorinated drinking water can result to cancer risk, specifically colorectal and bladder cancers that are caused due to the presence of THM and HAA (Cantor, 1997; Villanueva et al., 2004; Savitz et al., 2005; Villanueva et al.,

2014). In order to reduce the exposure of consumers to these adverse effects and at the same time, maintaining the standard of water quality and prevent the occurrence of pathogens, the regulatory authorities, i.e. World Health Organization (WHO), European Union (EU), United State Environmental Protection Agency (US EPA) and Nigerian Standard for Drinking Water Quality (NSDWQ) and in most developing countries, have introduced the drinking water guidelines and standards (EU, 1998; USEPA, 2006; WHO, 2006a, 2006b, 2008b; Villanueva et al., 2014). About 74 emerging DBPs (unregulated) have been reported by Water Research Foundation (Richardson et al., 2007; WRF, 2017) due to reaction of chemical oxidants used as disinfectants and raw water located in polluted area (Ma et al., 2012; Leavey-Roback et al., 2016; Li et al., 2018; Huang et al, 2018). For close to a decade a number of countries have abolished the use of chlorine for water treatment and substituted it with ozone, chloramine and chlorine dioxide in order to comply with the regulations (Russell et al., 2012; WRF, 2017). Consequently, these substitutes have been found to decrease the

formation of the controlled DBPs and served as precursor for the unregulated and emerging DBPs (Table 1).

The formation of different types of DBPs in drinking water was based on the reactions of the individual disinfectants with iodide and bromide as well as natural organic matters present in the water (Richardson *et al.*, 2007). Haloacetic acids (HAAs), trihalomethanes (THMs) and halogenated acetaldehydes (HALs) are the prominent classes of DBPs present in chlorinated water and they are regulated by US EPA, WHO and NSDWQ (Bischel and von Gunten, 2000; Zwiener & Richardson, 2005; Krasner *et al.*, 2006) for safety purposes and availability of quality drinking water. The presence of iodinated DBPs as well as nitrosamines in chloraminated drinking water has been reported by Richardson *et al.* (2007) and Boyd *et al.* (2011). Although, the use of ozone suppressed the formation of emerging DBPs, yet a small quantity of NDMA could still be produced in its reactions with polyelectrolytes (Padhye *et al.*, 2011; Yahaya, 2019). Weinberg *et al.*, (2006) and Jeong *et al.*, (2015) reported the presence of emerging DBPs such as halogenated DBPs, nitrogen and iodine containing ones, in treated water at lower concentration and were highly toxic than the regulated DBPs. The regulatory authorities in

Australia, Canada and WHO have set guideline values for emerging DBPs such as NDMA (Wang *et al.*, 2015). Emerging DBPs such as iodo and bromonitromethanes, brominated trihaloacetaldehydes, iodo-THMs, and haloamides are volatile and thermally unstable (Richardson, 2003). Hence, they require specific analytical methods (Chen *et al.*, 2002; Wang *et al.*, 2015).

In view of DBPs peculiar nature of polarity, thermal instability and volatility, no unique analytical method to date have been found for these analytes. This underscores the need to investigate possible analytical methods. To address this knowledge gap, this study reviews the existing analytical methods of sampling preservation, extraction techniques such as Liquid-liquid extraction (LLE); Solid-phase extraction (SPE); Solid-phase micro-extraction (SPME), Micro liquid-liquid extraction (MLLE), dispersive liquid-liquid microextraction (DLLME), SPME in headspace mode, headspace solid phase micro-extraction (HS-SPME), hollow fiber solvent bar micro extraction (HF-SBME) and derivatization as well as instrumentals techniques. An overview of the present methodologies and limitations to the analysis of DBPs have been presented.

Table 1: List of selected unregulated and regulated DBPs of priority contaminant.

| Unregulated Halonitromethane | Unregulated Iodomethane | Regulated Nitrosamines |
|-------------------------------------|---------------------------------|---------------------------------|
| Halonitromethanes | Dichloriodomethane | N-Nitrosodimethylamine |
| Chloronitromethane | Bromochloriodomethane | N-Nitrosopyrrolidine |
| Bromonitromethane | Dibromiodomethane | N-Nitrosopiperidine |
| Dichloronitromethane | Chlorodiodomethane | N-nitrosomethylethylamine |
| Dibromonitromethane | Bromodiodomethane | N-nitrosodiethylamine |
| Bromochloronitromethane | Iodoform | N-nitroso-di-n-butylamine |
| Trichloronitromethane | Dichloromethane | N-Nitrosodi-n-propylamine |
| Bromodichloronitromethane | Bromochloromethane | Unregulated Nitrosamines |
| Dibromochloronitromethane | Dibromomethane | N-Nitrosomorpholine |
| Tribromonitromethane | Unregulated Acetonitrile | N-Nitrosodiphenylamine |
| Unregulated Iodo-acids | Bromodichloroacetonitrile | Regulated Halo-methane |
| Iodoacetic acid | Dibromochloroacetonitrile | Bromodichloromethane |
| Bromoiodoacetic acid | Tribromoacetonitrile | Bromoform |
| (Z)-3-Bromo-3-iodopropenoic acid | Dichloroacetaldehyde | Chlorodibromomethane |
| (E)-3-Bromo-3-iodopropenoic acid | Dichloroacetaldehyde | Chloroform |
| 2-Iodo-3-methylbutenedioic acid | Bromochloroacetaldehyde | Chloroacetic acid |
| Other halo-acids | Tribromoacetaldehyde | Bromoacetic acid |
| Bromochloroacetic acid | Chloroacetaldehyde | Dibromoacetic acid |
| Bromodichloroacetic acid | unregulated and emerging DBPs | Dichloroacetic acid |
| Dibromochloroacetic acid | Hexachlorocyclopentadiene | Trichloroacetic acid |
| Tribromoacetic acid | Tetrachlorocyclopentadiene | Bromate |
| 2,2-dichloro-4-oxopentanoic acid | Cyanogen chloride | Chlorite |

(USEPA, 2006; Richardson *et al.*, 2007; Carlton & Schug, 2014; Wang & Mitch, 2015; Wang *et al.*, 2015; Bei *et al.*, 2016)

2. Sample Preservation and Chemical Quenching During DBP Analysis

Addition of suitable chemical preservative as quenching agent is required for good analytical procedure and accurate determination of regulated and unregulated DBPs as well as to stop the reaction between disinfectants, organic and inorganic substances (Kristiana et al., 2014; Gong et al., 2016). Quenching agent is a reducing agent that prevents the disinfectants (oxidizing agents) from further reactions (Kristiana et al., 2014). Addition of ammonium chloride is required to quench the residual chlorine but led to the conversion of chlorine residue to chloramine (Kristiana et al., 2014). The use of sodium arsenite is harmful (Reckhow, 2012) and may not reduce the rate of combination of free chlorine (Li et al., 2011) leading to DBPs formation. The ascorbic acid speed up decomposition of brominated trihaloacetonitriles (TCAN) and brominated trihalonitromethanes (THNM).

Hydrogen peroxide (Li et al., 2011) can be used to reduce combination of free chlorine but not tested for THM analysis (Chinn et al., 2013). It is also used as quenching agent for DBPs such as nitrosamines, cyanogen halides and iodinated DBPs but there is possibility of ammonia being produced in water in the presence of ascorbic acid (Weinberg, 2009) however, under a controlled condition it could be used to prevent further reaction of chlorine and chloramines for instant analysis of volatile and semi-volatile halogenated DBPs, this shows that there is the need for proper understanding of chemistry of DBPs in water for suitable analytical methods for adequate quantification of analyte of interest (Weinberg, 2009) Samples to be analyzed for haloacetonitriles (HAN) should be acidified with concentrated HCl to pH 6 as to slow down the base-catalyzed decomposition of HAN (Yu and Reckhow, 2015). In order to reduce the loss of analyte such as HCN and TCAN as well as to maintain the stability, phosphate buffer of pH 6 can be used (Yu and Reckhow, 2015). Sodium sulfite could be used to preserve analysis of chloral hydrate (Kristiana et al., 2014). However, previous studies reported the use of different preservatives without stating their limitations, but some were contradictory. For instance, sodium thiosulfate was used to preserve regulated DBPs by Chu et al., (2013) but Guilherme and Rodriguez (2015) and Pan et al. (2016) emphasized the use of NH_4Cl for all analytes.

3. Methods of Extraction

Several methods used for the extraction and analysis of regulated and unregulated DBPs are summarized in Table 2.

3.1 Liquid-liquid extraction (LLE)

The use of a suitable solvent in the extraction of DBPs plays a significant role in the efficiency of the extraction technique. Liquid-liquid extraction based on the solubility of two immiscible liquids polar and non-polar solvents was formerly used for stability studies. (Bond et al., 2015; Pan et al., 2016; Huang et al., 2017). It is cheap, fast and all samples can be extracted at once. Its limitations include the stress of using the procedure and exposure of the analyst to dangerous chemicals, such as methyl tert-butyl ether (MBTE) and pentane (Liew et al., 2012b; Akbarzadeh et al 2016).

3.2 Solid-phase extraction (SPE)

The technique results in a more quantitative extraction, saves time, while the small volume of solvent is used, it is automated and good quality control of complex sample matrix. The sorbent made of silica-SAX (Trimethyl ammonium chloride) for the analysis of HAA is better substitute to LLE (Waseem & Abdullah, 2010). An Bond Elut SAX- SPE sorbent could be used for the analysis of DBPs (Smith & Lynam, 2010). However, it is expensive, less efficient in the analysis of dihaloacetaldehyde and requires adequate training of the chemical analyst prior to handling of the instrument (Ding and Rogers, 2010; Chinn et al., 2013).

3.3 Solid-phase micro-extraction (SPME)

SPME method uses a fiber coated with a silica for adsorption of the DBPs (analyte) from the water sample, after then the fiber is placed into GC injector at a suitable temperature for the desorption of the organic pollutants into the column. It could be used for hydrophobic DBPs (Richardson, 2001) and various types of analytes such as PCBs, pesticides, PAH and phenols. In addition, the apparatus is simple and no solvents are required, better extraction of THM with SPME containing fused silica fibre and poly (dimethylsiloxane coating) detection limit below 2.8 $\mu\text{g/l}$, signal to noise ratio 3:1 and maximum extraction time of 20 minutes (Alexandrou et al., 2015). Also, SPME has better recovery than SPE in all target compounds but it is expensive (Alexandrou et al., 2015).

3.4 Micro liquid–liquid extraction (MLLE)

This is an extraction technique that involves the use of small volume of extraction solvent and sample, as small as 200 mL and 12 mL, respectively. It reduces the cost of analysis, yields better sensitivity and less environmental pollution, but its application is most suitable for an analyte present at a very low concentration, e.g., halo-ketones (Spietelun *et al.*, 2013; Serrano *et al.*, 2014).

Several micro extraction techniques, such as headspace single-drop microextraction (HS-SDME), dispersive liquid–liquid microextraction (DLLME), SPME in headspace mode headspace solid phase micro-extraction (HS-SPME), hollow fiber solvent bar micro extraction (HF-SBME) have been used for the analysis of DBPs and they have similar advantages as MLLE. The demerits of these methods are slow rate of extraction process in HS-SDME (Correa *et al.*, 2015). Cho *et al.* (2003) determined concentration of THM in potable water, they used HS-SPME with different cartridges and reported that 85-CAR/PDMS fiber contained the most appropriate coating due to its ability to extract large quantity of the analytes of interest. The efficiency of HS-SPME depends on the suitable coating and the type of the analytes (Cancho *et al.*, 2002). DLLME is a complex procedure and introduces impurity from extractant phase to the analyte (Anastassiades *et al.*, 2003; Al-Shatri *et al.*, 2014). A short optimal time with trifluoroacetic anhydride (TFAA) and *n*-octanol as derivatizing and extracting solvents respectively with DLLME (Al-shatri *et al.*, 2014). HS-SPME, the fibre is easily damaged and the surface is coated with a little extractant mixture (Spietelun *et al.*, 2013; Jiang & Ouyang, 2015). In addition, a longer optimal time was required for analytes with higher molecular weight (Bahri and Driss, 2010; Kristiana *et al.*, 2012).

3.5 Derivatization.

Derivatization is the chemical conversion of a specific functional group in a compound of interest to the conforming reaction group (s) in the new compound based on the derivatization reagent such as pentafluorobenzyl hydroxylamide hydrochloride (PFBHA), trimethylsilyl (TMS) dinitrophenylhydrazine (DNPH) and diazomethane and then, the extraction of the DBPs with a high polar solvent (MTBE) for suitable analytical method in GC (Le Lacheur *et al.*, 1993; Richardson *et al.*, 1999b) A compound that has poor thermal stability is converted to a thermal stable compound after derivatization. Other advantages of derivatization are increased volatility, increased molecular

weight for better peak separation and a decrease in absorption for good results (Saraji & Bidgoli 2009; Restek, 2012). Their shortcoming includes time, energy consumption, and hazardous chemicals. In addition, different by-products are produced (Richardson, 1998; Richardson *et al.*, 1999a; Richardson *et al.*, 2000) There are three types of derivatization namely, silylation, acylation and alkylation. Alkylation reagents decrease the polarity of a compound by substituting the active hydrogen such as phenols and carboxylic acids. Acylation produces an electron capture group, thus facilitating easy detection of the analyte of interest. It produces less polar compounds and improves volatility. It is mostly used in the analysis of drugs and compounds with many functional groups like carbohydrates, phenol and amine (Puig & Barceló, 1996; Restek, 2012). Silylation reagents with an alkylsilyl group such as trimethylsilyl (TMS) or tert-butyl dimethylsilyl (tert-BDMS) substitute the active hydrogen. They are most widely used because they help to decrease polarity and increase thermal stability and volatility of the analytes, e.g. alcohols, phenols, carboxylic acids, amines, and amides but less effective for the derivatization of amino group except with the use of trimethylchlorosilane as catalyst (Kataoko 1996; Puig & Barceló, 1996).

For instance, analysis of HAA with methanol in sulphuric acid as derivatizing agent was recommended by EPA method (2005) but excess ethanol prevent volatilisation of the target analytes (Cardador *et al.*, (2008). Dimethylsulphate (DMS) and tetrabutylammonium hydrogen sulphate (TBA-HSO₄), as derivatizing and ion pairing reagents respectively have been reported for effective use in the determination of HAA and single extraction of both THM and HAA in static headspace (SHS)-GC-MS (Cardador *et al.* (2008) and (2015). Furthermore, determination of the halo acetaldehydes (HALs) in water with pentafluorobenzyl hydroxylamine (PFBHA) as the derivatizing agent, yielded artifact with the surrogate (Jeong *et al.*, 2015) 5-chloro-2,2,3,3,4,4,5, 5-octafluoropentyl chloroformate a new derivatizing agent has a better extracting efficiency for highly polar DBPs than 2,2,3,3,4,4,5,5-octafluoropentyl chloroformate (Vincenti *et al.*, 2010; Yang and Zhang, 2016).

Table 2 : Summary of methods of extraction and analysis of regulated and unregulated DBPs.

| Sample Type | Vol. of Sample (mL) | Residual Cl test (mg/L) | Preservative | Extraction | Methods of Analysis | Analytes | LOD (µg/L) | LOQ (µg/L) | RSD (%) | Recovery (%) | Reference |
|--------------------------------------|-----------------------|-------------------------|--|---------------------------------|---------------------|--|-----------------------------|---------------------------|---------|--------------|-----------------------------|
| Swimming pool | 40 / (1L for NDMA) | 3.17 | NH ₄ Cl and Thiosuphate (for NDMA) | SPME & CH ₃ Cl(NDMA) | GC-MS | THM, HAA, HAN, HNM NDMA, HK | 0.6 -0.03 µg/m ³ | 2-0.097 µg/m ³ | NR | NR | Tardif et al., 2016 |
| Swimming pool | 50 | NR | H ₂ SO ₄ | SPE | MCE-CCCD | DCAA and TCA | 2.1 -2.7 mg/L | NR | 1.8–3.9 | NR | Ding & Rogers, 2010 |
| Water Treatment Plant | NR | 1.71 | NH ₄ Cl | SPME | GC-MS | THMs, HAA, HAN, CPK, HKs | NR | 0.01-3.6 ng/L | NR | 95 | Guilherme & Rodriguez, 2014 |
| Raw and treated water | 500 mL | NR | Formic Acid | SPE | LC-MS | Haloquinones : DCBQ, DCMBQ, TCBQ, and DBBQ | 0.5-1.7 ng/mL | 1-6 ng/L | 1-15 | 84 | Zhao et al., 2010 |
| Tap, surface and swimming pool water | NR | NR | NR | NR | HPLC / ICP-MS | IO ₃ ⁻ , MIAA, CIAA BIAA, I ⁻ , DIAA, BrO ₃ ⁻ , MBAA, Br ⁻ , BCAA, DBAA, BDCAA, DBCAA, TBAA. | 0.33 - 3.28 µg/L | NR | 0.2-2.8 | 67 -123 | Shi & Adams, 2009 |
| Drinking water | 40 | NR | Ascorbic acid | SADLLME | GC-MS | MCAN,MBAN, MIAN DCAN, DBAN, BCAN TCAN | 0.4 -13.3 ng/L | 1.2-43.9ng/L | <10.2 | 73-105 | Ma et al., 2014 |
| Tape water | 60 | NR | Ascorbic acids | LLE/MTBE | GC-ECD | THMs, THAs, HANs and HKs | 0.04 - 22 mg/L | NR | NR | NR | Huang et al., 2017a |
| Water Treatment Plant | 500 | 1.0 | Ascorbic acids | LLE-MTBE | GC-ECD | HAAAs THMs, HNMs, I-DBPs, I-HAMs and I-THMs | <10 µg/L | NR | NR | NR | Zhang et al., 2017 |
| River water | 40 | NR | Ascorbic acids | LLE-MTBE | GC-ECD | HAcAms, HANs, and THMs | 0.04 - 0.22ug/L | NR | NR | NR | Huang, et al., 2017b |
| Tap water | 1L | 0.9 | Na ₂ SO ₃ | LLE-MTBE (100mL) | UPLC/ESI-MS | CIAA, DIAA, IHMB, DINP, DINP, DIHB, TIP | 0.03 –0.5 ng/L. | NR | NR | NR | Pan et al., 2016 |
| Drinking Water | NR | NR | C ₆ H ₇ O ₆ Na | LLE-MTBE | GC-MS | BCAcAm, DBAcAm, DCAcAm, BAcAm, DBAcAm | 0.1 - 0.2 µg/L | NR | <20 | NR | Kosaka et al., 2016 |
| Water Treatment plant | 60 | NR | KH ₂ PO ₄ , Na ₂ HPO ₄ & ascorbic acid | HS SPME | GC-MS | HN: MCAN, MBAN, DCAN, DBAN, BCAN, TCAN,DCPN, DBBN | 0.9 – 80 ng/L | NR | 3.8 –12 | 90-102 | Kristiana et al., 2012 |
| Tap, ground and surface water | 1L | 1.7 | ascorbic acid, NH ₄ Cl Na ₂ SO ₃ | LLE-MTBE | GC-MS | BCNM DCNM BDCNM DBCNM TBNM TCNM BAAm CAAm DBAAm | 0.08 - 6 µg/L | NR | 4 -31 | >90 | Liew et al., 2012 |

DCAAm TCAAm

| | | | | | | | | | | | |
|----------------|-----|----------|---------------------------------|----------|--------|---------------------------------------|---------------------|----|----------|-------|---------------------|
| Drinking water | 500 | 1.4 mg/L | Na ₂ SO ₃ | HFSBME | GC-ECD | CF, DCBM, CDBM, BF | 0.017 – 0.037 ng/mL | NR | 5.7–10.3 | 74-91 | Correa et al., 2015 |
| Drinking water | 1L | NR | NH ₄ Cl | LLE-MBTE | GC-ECD | HANs, HAcAms, THM4, DCAN, BCAN, DBAN. | 1.9 - 3.8 µg/L | NR | NR | NR | Bond et al., 2015 |

Chloroacetonitrile (MCAN), Bromoacetonitrile (MBAN) , Dichloroacetonitrile (DCAN) , Dibromoacetonitrile (DBAN), Bromochloroacetonitrile (BCAN), Trichloroacetonitrile (TCAN) , 2,2-Dichloropropionitrile (2,2-DCPN) 2,2-Dibromobutyronitrile (2,2-DBBN) Salt-assisted dispersive liquid–liquid microextraction (SADLLME) Microchip capillary electrophoresis with capacitively coupled contactless conductivity detection (MCE-CCCD) Pentafluorobenzylhydroxylamine (PFBHA), 2,6-dichloro-1,4-benzoquinone (DCBQ); 2,6-dichloro-3-methyl-1,4-benzoquinone(DCMBQ), 2,3,6-trichloro-1,4-benzoquinone (TCBQ) and 2,6-dibromo-1,4-benzoquinone (DBBQ). Dimethylsulfamide (DMA) ; Nitrosodimethylamine (NDMA) HAcAm9, 9 haloacetamides; Cl-HAcAms, chlorine-containing HAcAms; CAcAm, chloroacetamide; DCACAm, dichloroacetamide; TCACAm, trichloroacetamide; Cl-, Br-HAcAms, chlorine- and bromine-containing HAcAms; BCACAm, bromochloroacetamide; BDCACAm, bromodichloroacetamide; DBCACAm, dibromochloroacetamide; Br-, HAcAms, bromine-containing HAcAms; BACAm, bromoacetamide; DBACAm, dibromoacetamide; TBACAm, tribromoacetamide, Monobromoacetic acid (MBAA) Monoiodoacetic acid (MIAA), Bromide (Br-)Bromochloroacetic acid (BCAA) Dibromoacetic acid (DBAA) Chloroiodoacetic acid (CIAA) Bromoiodoacetic acid (BIAA) Iodide I- 1Diiodoacetic acid (DIAA) Bromodichloroacetic acid (BDCAA) Dibromochloroacetic acid (DBCAA) Tribromoacetic acid (TBAA) Monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), bromochloroacetic acid (BCAA), trichloroacetic acid (TCAA), tribromoacetic acid (TBAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), Trifluoroacetic anhydride (TFAA), Single-drop microextraction (SDME) Trihalomethane formation potential (THMFP)Total organic carbon (TOC), Natural organic matter (NOM) Trichloromethane (TCM), Bromodichloromethane (BDCM), Dibromochloromethane (DBCM) and Tribromomethane (TBM). Not registered (NR).

4. Instrumental methods of analysis

Several instruments are employed for the analysis of DBPs. These include; GC-ECDs, GC-MS, liquid chromatography mass spectrometry (LC-MS), liquid chromatography ultra violet (LC-UV), and ultra-high-performance liquid chromatography mass spectrometry (UHPLC-MS) respectively.

The GC-ECD operates based on the ability of the organic compound to capture a thermal electron and form a negatively charge ions. The electron loss is proportional to the quantity of analyte in the sample (Poole, 2013; Poole, 2015). The GC-ECD has been widely utilized for the analysis of DBPs in drinking water and with a detection range from 1.9 - 3.8 µg/L and 0.017 – 0.037 ng/mL (Correa et al. 2015). However, ECD can only be utilized to determine the amount of an analyte present in the sample but not for an identification. This is because there is no library match to suggest the likely emerging compounds (Waseem & Abdullah, 2010)

GC-MS is used for the analysis of volatile, semi-volatile, less polar and low molecular weight DBPs, such as: HAA, THM and HACN (Richardson, 2001) Previous study revealed a good precision and linearity in the analysis of DBPs (regulated and unregulated) in water samples (Kristiana et al., 2012; Kosaka et al., 2016). However, it cannot be used for the identification of high polar carbonyl compounds with many functional groups e.g. ketone and aldehyde (Richardson et al., 2000; Kosaka et al., 2016).

UV measures the intensity of light absorbed by the sample at various wavelengths to identify the analyte. It is coupled with high performance liquid chromatography to measure the amount and identify the analyte contained in the sample (Berger, 2017). HPLC is used to isolate, detect, and measure individual component in a sample mixture. It operates under the high pressure pump and pass the solvent sample mixture over a column containing solid adsorbent at various flow rates resulting into the separation of each component as they are eluted from the column (Gerber et al., 2004; Berger, 2015). It has a wide range of application due to its high sensitivity and selective isolation, but takes time in the analysis of some samples (Gerber et al., 2004; Upadhyay et al., 2015). Liquid chromatography mass spectrometry (LC-MS) operates similarly like HPLC/MS but at low pressure (Zhao et al., 2010b). Both of them are used for the analysis of high molecular weight, polar, highly polar N-DBPs and DBPs that dissociates at high temperature (Ding and Chu 2017). It can also be

used for the analysis of HNM, nitrosamine, and haloquinones (Zhao et al. 2010b; Chu et al. 2013). Their limitations are choice of mobile phase and suitable oven conditions for analysis. Tolerable delay time is exceeded and absence of library search for the identification of emerging compounds, however, the triple quadrupole (QqQ) analyzer could be used (Boucherit et al., 2015).

5. Conclusion

An overview of the analytical methods has shown areas of optimizing the methods. Of all methods of extraction of DBPs SPE is more convenient, yielding a high extraction efficiency with a lower detection limit. It is a well-known fact that GC-ECD and GC-MS are frequently used which shows that a volatile, semi-volatile, less polar and low molecular weight of regulated and unregulated DBPs are analyzed. The review identified an irregularity in the use of chemical preservative, the environmental unfriendliness of MBTE used in LLE and inappropriate use of chemical preservatives. These research areas require further investigation. It was also discovered that GC-MS that is mostly used for the analysis of regulated and unregulated DBPs may not be appropriate for the analysis of highly polar compounds. The high sensitive analytical instruments such as: GC-ECD, HPLC and LC/MS have no library database to determine new DBPs. Attention should focus on high molecular weight, emerging unregulated and highly toxic DBPs with a moderate occurrence in water.

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Conflict of interest

The authors declare no conflict of interest.

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