OPTIMIZATION OF METHODS FOR THE DETERMINATION OF DBPs

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ABSTRACT
Chloroform and other bromochlorotrihalomethanes were first identified as disinfection byproducts (DBPs) in chlorinated water in 1970s. Since then, many other DBPs have been identified such as haloacetonitriles, haloacetaldehydes, cyanogen halides, aldehydes, ketoacids, chlorite, bromate and other organic and inorganic compounds. Due to their occurrence and potential health risks, the U.S.EPA promulgated the Stage I Disinfectants and Disinfection Byproducts (D-DBP) Rule in 1998. To assist water utilities monitoring DBPs in their finished water, the U.S. EPA published a list of approved analytical methods under the D-DBP Rule. In 1996, the U.S. EPA also promulgated the Information Collection Rule (ICR) to collect brackground information on DBPs and pathogens for the Stage II D-DBP-Rule. Actually 500 DBPs are known but few have been investigated for their quantitative occurrence and health effects. Due to the fact that their identification and quantitation have become extremely important to drinking water companies in order to reduce or remove their presence, other analytical methods different from those proposed by U.S. EPA have been optimized and are now commented in this article.

INTRODUCTION
Chlorine, ozone, chlorine dioxide and chloramine are the most widely used disinfectants in drinking water disinfection. Despite their benefits for the improvement of water quality, disinfection by-products (DBPs) are formed due to the interaction of aqueous free disinfectants with natural organic matter. In addition, high bromide levels in water reservoirs used as sources of drinking water, can significantly contribute to the formation of brominated and mixed bromo/chloro-DBPs during chlorination. Trihalomethanes (THMs) were identified as the main DBPs more than 30 years ago (Rook, 1974; Bellar *et al.*, 1974). Later, other DBPs such as haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), haloaldehydes, chlorinated phenols, chloropicrin (CP), cyanogen halides (CNX) and chloral hydrate (CH) were also reported (Krasner *et al.*, 1989; Stevens *et al.*, 1989; Peters *et al.*, 1991). Actually 500 DBPs are known but few have been investigated for their quantitative occurrence and health effects.

The presence of DBPs in drinking water is a matter of concern for human health and can also produce unpleasant organoleptic taste. For this reason, the occurrence of these

DBPs in USA and Canadian water treatment plants (Lebel *et al.* 1997) has been studied and legislation has been established. Under Stage I of the Disinfectants/Disinfection By-products (D/DBP) Rule, USEPA sets maximum contaminant levels (MCLs) for total trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane and bromoform) at 80 μg l^{-1}; for a total of five haloacetic acids (monochloroacetic, dichloroacetic, trichloroacetic, monobromoacetic and dibromoacetic acids) at 60 μg l^{-1}; for bromate at 10 μg l^{-1} and for chlorite 1.0 mg l^{-1}. Other DBPs have been added to the US Environmental Protection Agency's Candidate Contamination List (CCL), which is the list from which future regulated drinking water compounds will be selected (Fed. Register, 1998; USEPA, 1998a). In Europe, the 98/83/CEE Directive is less restrictive than that applied in the USA. The only DBPs to be controlled are the four trihalomethanes, the proposed maximum level being 100 μg l^{-1}.

Under typical disinfection conditions, the known DBPs only account for roughly 50% of total organic halogen (TOX) during chlorination, 28% of TOX during chlorine dioxide treatment, and 17% of TOX during chloramination (Zhang *et al.*, 2000). A significant portion of the unaccounted TOX can be attributed to highly polar or high molecular weight DBPs (Khiari *et al.*, 1996; Zhang *et al.*, 2002). Current areas of interest include the discovery of new DBPs in drinking water; the identification of higher molecular weight DBPs that are known to be present but have not been identified due to the lack of appropriate analytical methods for their determination; the detection of new DBPs related to taste-and-odor problems such as iodinated DBPs; as well as the study of N-nitrosodimethylamine (NDMA), identified recently as DBP from chloramine and chlorine disinfection (Richardson, 2002a).

Their identification and quantitation have become extremely important to drinking water companies in order to reduce their presence. The determination of trace concentration (at μg l^{-1} and/or ng l^{-1} levels) in drinking water is not a trivial matter due to the differences in the chemical structures, polarity, and volatility of DBPs. EPA methods are analytical methods for the regulated DBPs. Each EPA method purposely uses different techniques and equipment to accommodate the various skills and instruments available in compliance laboratories. These methods may also be used for some unregulated DBPs. Optimization of analytical methods and development of new methods are an important tool for identification of new DBPs and for their quantification. The objective of the present paper is to review analytical methods for the determination of common DBPs in drinking water. Several non-regulated DBPs are also included since they may be included in future regulations or used for treatment process control.

Trihalomethanes and non-volatile neutral halogenated fraction

Trihalomethanes (THMs) represent only the very volatile fraction of DBPs. EPA Methods 502.2, 524.2 and EPA 551.1 are the three official methods approved in the USA for these compounds (USEPA, 1995). EPA Method 551.1, based on liquid-liquid microextraction (MLLE) with methyl *tert*-butyl ether as extracting solvent and gas chromatography-electron capture detection (GC/ECD), allows to extract them from drinking water quantitatively (ca. 100%). The same behavior was observed for EPA 502.2 and 524.2, based on purge and trap (PT) for sample concentration, because THMs have high enough volatility and low enough water solubility to be efficiently removed from water samples with this technique, independently of the trap used (e.g. Tenax, Tenax/silica/charcoal or Vocarb 3000) (Cancho *et al.*, 2000a). EPA Method 502.2. employs photoionization and electrolytic conductivity detectors in series whereas EPA Method 524.2 method uses gas chromatograhy-mass spectrometry (GC/MS). Three analytical methods are also listed in Standard Methods -6232B, 6232C and 6232D- for THMs (Standard Methods, 1998). The first, which is similar to EPA 551.1, is based in LLE with n-pentane as organic solvent and GC/ECD detection. The Standard Methods 6232C

and 6232D are based on PT-GC/MS similar to EPA methods 524.2 and 502.2, respectively.

Other extraction methods such as headspace HS-GC/ECD, HS-GC/MS, closed loop stripping analysis CLSA-GC/ECD or CLSA-GC/MS (Kampioti, *et al.*, 1999; Cancho *et al.*, 2000a, Nikolaou *et al.*, 2002) have been used. HS-GC/ECD and HS-GC/MS are simple and reproducible methods that can be automated easily and avoid the use of solvents and production of wastes; however, low recoveries ranging from 17 to 27% have been reported (Cancho *et al.*, 2000a). Recently, it has been proved that the presence in drinking water of trichloroacetones, trihaloacetonitriles and trihaloacetic acids produced THMs upon heating aqueous solution at 60 ºC for 30 minutes in a headspace sampler; then, HS-GC/MS method overestimates the net concentration of THMs due to positive errors (Takahashi *et al.*, 2003). The recovery efficiency obtained for THMs with CLSA was higher than HS and ranged from 10 to 50% (Kampioti, *et al.*, 1999; Cancho *et al.*, 2000a); the CLSA recoveries are higher for the brominated THMs than for the chlorinated ones.

HACH® proposed in an application note a new method for the determination of THMs (Lord, 2004) where no extraction or concentration steps are required, and no hazardous materials are used or generated. It is a new colorimetric method that can be used to quickly adapt to changing influent water characteristics and to establish trending data for the formation of THMs throughout the distribution system. The mechanism of this test is as follows: In an aqueous sample, trihalogenated species react with n,n-diethylnicotinamide. The addition of potassium hydroxide and heat causes the n,n-diethylnicotinamide ring to cleave to form 5-hydroxy-2-(n,n-diethylcarboxamyde)-2,4-pentadienal. The latest reacts with 7-naphthalamine-1,3-disulfonic acid (G-amino acid). The Schiff base formed absorbs with a broad peak at 515 nm. This orange species follows Beers law and directly relates to the quantity of trihalogenated species present (four THMs; trichloro-, dichlorobromo-, chlorodibromo-, tribromo- acids; chloral hydrate; 1,1,1-trichloropropane and trichloroacetonitrile). In this application note, multiple samples from across the United States were analyzed and the accuracy, precision and equivalency of the new method were determining by comparing the new method results to the three EPA methods (524.2, 551.1 and 552.2).

Non-volatile neutral halogenated fraction is represented for haloacetonitriles (HANs), chloropicrin (CP), halogenated ketones (HAKs) and chloral hydrate (CH) as main compounds. Previous studies have shown that most of the mutagenic activity in chlorinated drinking water has been associated with non-volatile fraction, especially for haloacetic acids (HAAs) and HANs (Bull *et al.*, 1990). Quantitative extraction is achieved for neutral halogenated DBPs with EPA Method 551.2 and considering MtBE or n-pentane - if chloral hydrate is not analyzed- as extraction solvents. Extraction efficiency is increasing when sodium sulfate is used instead of sodium chloride since the latter contains traces of bromide ions, which by reacting with HOCl, could overestimate the brominated DBP concentration. In both cases, GC/ECD or GC/MS were used for identification and quantitation.

Cyanogen halides are commonly identified in chloraminated and also chlorinated waters. Cyanogen bromide (CNBr) was also identified as a byproduct in ozonated waters with high bromide concentration (West *et al.*, 1991). Several methods are described in the literature for cyanogen chloride (CNCl) (Xie and Hwang, 2000). The EPA method 524.2 allows the determination of cyanogen chloride but is unsatisfactory for the brominated analogue that requires a heated PT. A HS-GC/ECD procedure has been proposed for the simultaneous determination of both compounds with detection limits of 0.04 and 0.2 µg l^{-1}, for cyanogen chloride and bromide, respectively (Xie and Reckhow, 1993). Another

approach uses liquid-liquid microextraction followed by GC/ECD with detection limits of 0.13 and 0.26 µg l^{-1} for CNCl and CNBr (Sclimenti *et al.*, 1995). Solid-phase microextraction (SPME) using a DVB/CAR/PDMS (divinylbenzene/ Carboxen/ polydimethylsiloxane) fiber has been proved suitable for the simultaneous determination of CNCl and CNBr with detection limits of 0.077 and 0.041 µg l^{-1}, respectively (Cancho *et al.*, 2000b).

Odorous halogenated DBPs in drinking water.
Odors and tastes in drinking water are a matter of concern for water suppliers and a frequent source of complaints from consumers who mostly associate the presence of unpleasant odors and tastes with the possibility of health risk. The ECC Drinking Water Directive, related to the quality of water intended for human consumption, includes taste and odor parameters. Thus, water companies have to cope with qualitative and quantitative determinations. Among the eight odor groups described in the water flavor wheel, the earthy-musty odors are especially troublesome because they are particularly unpleasant and often encountered in water (Suffet *et al.*, 1996). Besides the well-known earthy-musty algae metabolites (e.g. geosmin and 2-methylisoborneol) (Rosen *et al.*, 1970; Burlingame *et al.*, 1986), attention was drawn to certain halogenated DBPs due to their low odor threshold concentrations in treated water. Among them, iodo-THMs and halogenated anisoles that can be formed by biomethylation of the corresponding halophenols initially formed during chlorination or chloramination practices have received much attention (UKWIR, 1996; Cancho et al, 1999). Reported odor threshold levels for iodo-THMs ranged from 0.003 µg l^{-1} (CHI$_3$) to 5.8 µg l^{-1} for CHCl$_2$I (Cancho *et al.*, 2001) whereas for chlorinated anisoles there are some discrepancies in the literature. Odor threshold values ranging from 0.7 pg l^{-1} (Curtis *et al.*, 1972) to 7 ng l^{-1} (Guadagni *et al.*, 1978) for 2,3,6-trichloroanisole and from 30 pg l^{-1} (Curtis *et al.*, 1972) to 50 ng l^{-1} for 2,4,6-trichloroanisole (Brownlee *et al.*, 1993) have been reported. In bromide rich waters 2, 4,6-tribromoanisole with an odor threshold of 30 pg l^{-1} (Malleret *et al.*, 2001) has been identified in treated waters whereas several chlorobromoanisoles had odor threshold average values of ~2 ng l^{-1} as recently reported (Diaz *et al.*, 2005a).

Iodinated DBPs can also be formed as a consequence of this interaction when iodine (i.e., from natural sources, seawater infusion, or brines) is present. The six possible iodinated trihalomethanes (ITHMs), related to pharmaceutical or medicinal odors in water, were previously synthesized due to the lack of reference standards and different analytical methods for their determination in water were evaluated: HS-GC/ECD, PT-GC/MS, CLSA-GC/MS, liquid-liquid microextraction MLLE-GC/ECD and SPME-/GC/ECD (Cancho et al, 1999; Cancho *et al.*, 2000a). Recovery ranges using HS-GC/ECD were <50% for all iodo-THM except for CHI$_3$ (0.1%) and from 66% (CHCl$_2$I) to 4% (CHI$_3$) when used PT-GC/MS. Improved recoveries were obtained using CLSA-GC/MS ranging from 47% (CHCl$_2$I) to 4% (CHClI$_2$) but the MLLE method, with methyl *tert*-butyl ether as extracting solvent, was the only method capable of extracting the six ITHMs quantitatively (recoveries around 100%) with relative standard deviation (RSD %) lower than 7% and limits of detection ranging from 10 to 30 ng l^{-1} (Cancho *et al.*, 2000a). The performances of several methods for the determination of the iodo-THMs in the US Nationwide DBP Occurrence Study has been compared (Weinberg *et al.*, 2002). They found higher quantification levels with LLE-GC/ECD than with PT-GC/MS for certain iodo-THMs that was attributed to coeluting interferences in the GC/ECD method. The former was considered the primary quantitation method and PT-GC/MS as the confirmation method if interferences occurred. Minimum reporting levels of 0.1-0.7 µg l^{-1} using LLE-GC/ECD and 0.2-0.5 µg l^{-1} for PT-GC/MS and SPME-GC/ECD for ITHMs were achieved (Weinberg *et al.*, 2002).
Other iodinated DBPs such as iodoalkanes and 4-iodophenol can be formed if iodine is used as an alternative to disinfect recycled water such as long-duration manned space

missions (Frazey *et al.*, 1998). They were determined by SPME using a polyacrylate coating, followed by GC/MS and GC/ECD to achieve limits of detection ranging from 0.4 to 120 ng l^{-1}.

The determination of odorous halogenated anisoles such as 2,4,6-tribromoanisole at pg l^{-1} levels has been accomplished by CLSA-GC/MS with large volume injection (LVI) (Malleret *et al.*, 2001). Other approaches using SPME-GC/ECD for the simultaneous determination of earthy-musty halophenols and their corresponding haloanisoles has been carried out with detection limits about 0.5 ng l^{-1} (Malleret *et al.*, 2003). A SPME-GC/MS method has been recently employed to identify chlorobromoanisoles at detection levels ranging from 0.03 ng l^{-1} (for 2,4,6-trichloroanisole) to 0.25 ng l^{-1} (for 2,3-dibromo-6-chloroanisole) in treated waters and distribution reservoirs (Diaz *et al.*, 2005b). Another solventless technique, stir bar sorptive extraction (SBSA), has been successfully applied to the analysis of trichloro- and tribromoanisoles at ng l^{-1} levels (Ochiai *et al.*, 2001; Benanou *et al.*, 2003).

Haloacetic acids

Haloacetic acids (HAAs) represent the second largest group of DBPs generated by water disinfection. There are 9 compounds: mono-, di- and trihalogenated (chloro or bromo) and mixed (chlorobromo-; dichlorobromo- and chlorodibromoacetic acids). HAAs are not regulated in Europe but for the sum of five of them (chloro-, bromo-, dichloro-, dibromo- and trichloroacetic acid), a maximum contaminant level of 60 µg l^{-1} is set at in USA (USEPA, 1998b). Drinking water utilities in the United States are not required to collect data on bromochloroacetic acid or the brominated trihaloacetic acids during compliance monitoring, but water utilities that are making changes in their treatment processes may want to collect data on the formation of all nine HAAs. This is because some treatment changes cause the speciation of HAAs to shift to the more brominated compounds (Gretchen, 1996).

There are three approved methods for HAA analysis: EPA methods 552.1, 552.2 and 552.3 and Standard Method 6251B (USEPA, 1998b; Standard Methods, 1998). HAAs are deprotonated (at 99%) under drinking water conditions, so they cannot be directly injected onto a column. Two steps are required for their determination. The first one is based on a solvent extraction using MTBE and an acidified sample solution. The second one, a derivatization process; methylating the carboxylate moiety is the standard approach to making these species amenable to GC (Urbansky, 2000). In EPA Method 552 and SM 6251B, hazardous diazomethane is used for methylation, and in more recent EPA Methods 552.1 and 552.2, acidified methanol was used for methylation. It has been found that the performance of these methylation methods (particularly for the brominated trihaloacetic acids, dalapon and the surrogate 2,3-dibromopropionic acid) is dependent on both the specific water tested and the analyst's skills and abilities (Xie, 2002).

The approved methods were shown to have little to no esterification efficiencies for the brominated trihaloacetic acids (HAA3), as it was described above. Although methylation with acidic methanol was determined to be more efficient and rugged than methylation with diazomethane, increasing acidic methanol volume and increasing methylation temperature are suggested to improve the incomplete methylation of HAA3. This modification of EPA method 552.2. or EPA 552.3 and the introduction of a new higher boiling solvent —tertiary-amyl methyl ether (TAME)— as an alternative to MTBE is reported, which has significantly improved methylation efficiencies for HAA3 (Domino *et al.*, 2004; USEPA, 2003). Using TAME, methylation efficiency for tribromoacetic acid was increased to 82% meanwhile 45% was obtained with MTBE; as a direct result, the new method has lower detection limits for HAA3 and markedly improved precision. The removal of copper sulfate in the initial extraction (which was shown to degrade HAAs) and the incorporation of extract neutralization (which greatly limits the possibility of

accidentally injecting acidic extracts) were two changes that have also been made to the new method.

A method capable of analyzing all nine HAAs and dalapon at µg l^{-1} levels has been developed (Xie, 2001). This GC/MS method gave cleaner baselines, had few interfering peaks and made use of a short run time without compromising the analytical results in comparison to EPA Method 552.2, which uses GC/ECD. The limit of detection was less than 1µg l^{-1} and the spiked recovery ranged from 73 to 165%.

A GC-ion trap mass spectrometric method (ITMS) for quantifying all nine HAAs in water (as well as plasma and urine) at 25-1000 pg ml^{-1} levels has been reported (Jia *et al.*, 2003). The method was based in the derivatization of HAAs with pentafluorobenzyl bromide and further detection with electron capture negative ion chemical ionization. An in-situ derivatization headspace SPME and GC/ITMS method has also been developed (Sarrion *et al.*, 2000) where derivatization of HAAs to methyl esters with dimethyl sulfate was improved by the addition of tetrabutylammonium hydrogen sulfate to the sample as ion-pairing agent. The CAR-PDMS fiber appeared to be the most suitable for their determination at detection limits ranging from 0.010 to 0.45 µg l^{-1} depending on the compound.

A chemical and biological characterization of iodoacid DBPs which represent a new class of potent drinking water contaminants has been performed (Plewa *et al.*, 2004). Their determination is important toxicologically because iodoacetic acid has been shown to induce neural tube closure defects and other developmental abnormalities in mouse embryos (Hunter and Tugman, 1995; Hunter *et al.*, 1996). Methylation derivatization with BF_3-methanol were used to enable the identification of iodinated carboxylic acid DBPs such as iodoacetic, bromoiodoacetic, (*Z*) and (*E*)-3-bromo3-iodopropenoic and (*E*)-2-iodo-3-methylbutenedioic acid with GC/MS in drinking water samples from source water with high concentrations of bromide and iodide that was treated with chloramines (Richardson *et al.*, 2003).

Haloacetic acids have been also analyzed by LC/MS with negative ion electrospray (ESI) (Hashimoto *et al.*, 1998; Takino et al, 2000; Loos and Barceló, 2001) or ESI of stable association complexes to reduce problems with brominated trihaloacetic acids (Magnuson and Kelty, 2000a). Volatile ion-pairing reagents such as tributylamine (Takino *et al.*, 2000) or triethylamine (Loos and Barceló, 2001) were employed to detect HAAs in the low µg l^{-1} level.

Due to the fact that HAAs exist as anions in drinking water, ion chromatography (IC) is an obvious choice for their separation and detection. As it no requires no sample derivatization, IC in its various modes, such as ion-exchange, ion-interaction and ion-exclusion chromatography, is increasingly being investigated as a simpler alternative to gas chromatographic methods for the determination of polar DBPs in drinking waters (Paull *et al.*, 2004). Detection limits quoted for the regulated HAAs are commonly in the mid to low µg l^{-1} range, however, in most cases analyte preconcentration is still necessary for detecting them in actual drinking waters. The coupling of IC to ESI/MS provides a potential future direction, with improved sensitivity and selectivity compared to conductivity based detection. However, associated cost and complexity for routine analysis is currently relatively high (Paull *et al.*, 2004). Three methods for the on-line monitoring of HAAs in distribution systems: nicotine-fluorescence flow injection analysis (NCA-FL-FIA), an ion-chromatography with membrane suppressed conductivity detection (IC-MSCD) and a post-IC column NCA-FL method have been investigated (Emmert et al, 2004a). Preliminary results shows that HAAs can be analyzed over the concentration range from ~5 to 100 µg l^{-1}. Other alternative approaches for the determination of HAAs in water such as capillary electrophoresis (CE), capillary zone electrophoresis (CZE) and spectrophotometric methods as well as GC/MS and HPLC/IC/LC/MS methods have been recently reviewed (Emmert *et al.*, 2004b).

Carbonyl DBPs
The majority of organic DBPs formed as ozonation byproducts are aldehydes, but other DBPs include ketones, keto-aldehydes, carboxylic acids, aldoacids, ketoacids, hydroxy-acids, alcohols, esters and alkanes (Haag *et al.*, 1983;Glaze, 1986; Glaze et al, 1989; Coleman *et al.*, 1992). Small polar aldehydes and ketones (such as formaldehyde, glyoxal and acetone) and also dicarbonyl compounds have been extracted from water by pentafluorobenzylhydroxylamine (PFBHA) derivatization followed by LLE (Glaze *et al.*, 1989), SPE (Yamada and Soniya, 1989), PT (Yang *et al.*, 1995) or SPME (Bao *et al.*, 1998; Martos and Pawliszyn, 1998; Keszler et al, 1998; Cancho *et al.*, 2002). PFBHA reacts with the carbonyl group and imparts nonpolar character to carbonyl-containing molecules, allowing them to be extracted from water and analyzed (Glaze et al, 1989; Yamada and Soniya, 1989). This procedure works well for those compounds that are amenable to form a product amenable to GC/ECD or GC/MS (EI mode). EPA methods 556, 556.1 and Standard Methods 6252 (USEPA, 2000; Standard Methods, 1998) are based on PFBHA derivatization of aldehydes to get the corresponding oximes which are then extracted with n-hexane and analyzed by GC/ECD. A method employing PFBHA and diazomethane derivatization to quantify glyoxylic acid in solutions of ozonated fulvic acid has been reported (Xiong *et al.*, 1992).

Analytical difficulties arise from the high polarity, hydrophilicity and instability of the ozonation by-products, such as those with multiple hydroxyl or carboxyl groups, consequently this method is not always effective. For example, molecular ions are usually small or are not present for PFBHA derivatives (especially for hydroxy-substituted aldehydes and ketones, but also for many unsubstituted aldehydes and ketones). Some aldo- and ketoacids, such as glyoxylic, pyruvic and ketomalonic acid, cannot be observed using only PFBHA derivatization and GC/MS analysis (Xie and Reckhow, 1997). In addition, for compounds with multiple carbonyl groups, analysis by PFBHA-GC/MS can be difficult due to the increased lack of volatility with each additional derivatizing group on the carbonyls. Recently, researchers have proposed double-derivatization/GC/MS methods for some highly polar chemicals in order to obtain molecular weight information and improved chromatography. One of these methods (Xie and Reckhow, 1997) employed GC/MS combined with PFBHA-diazomethane double derivatization to identify ketoacids in ozonated waters; three ketoacids, glyoxylic, pyruvic and ketomalonic acids, four aldehydes and two analytical artifacts were identified. Another method measured hydroxy carbonyls and other carbonyls in air by PFBHA, further reacting the PFBHA derivatives of hydroxy carbonyls with bis (trimethylsilyl)-trifluoroacetamide (BSTFA) and detecting the derivatives with GC/ITMS which results effective for hydroxy-ketones and aldehydes (Spaulding *et al.*,1999). Other approaches use LC/MS with ESI ionization to analyze derivatized carbonyl DBPs. A qualitative method using 2,4-dinitrophenylhydrazine (DNPH) derivatization followed by analysis with LC/ESI-MS (negative mode) was developed for determining highly polar aldehydes and ketones in ozonated drinking water as well as from disinfectants other than ozone (Richardson *et al.*, 2000). The detection limits for the DNPH-LC/MS method are not as low as for the PFBHA-GC/MS, and then its replacement is not recommended. A similar approach using DNPH and LC/ESI-MS/MS has been used to investigate carbonyl polar DBPs (Zwiener *et al.*, 2002, 2003). Tandem mass spectrometric experiments like precursor ion scans at m/z 163 for aldehydes, m/z 152 for ketones and m/z 182 for dicarbonyls and hydroxycarbonyls facilitate the identification of several multifunctional carbonyls in treated water. However, neither DNPH nor DMNTH [4-(dimethylamino)-6-(4-methoxy-1-naphtyl-1,3,5-triazine-2-hydrazyne] employed to analyze carbonyl DBPs by LC/API-MS are suitable reagents for halogenated carbonyl compounds due to side-reactions of the hydrazine based regents because of the chlorine substitution by derivatizing agents (Richardson *et al.*, 2001). A suitable alternative, CHMA (O-(carboxymethyl)

hydroxylamine)) does not affect the chlorine and the formed oxime derivatives give ESI spectra and CID-MS with fragments of the CMHA moiety and diagnostic fragments of the carbonyl moiety (Richardson *et al.*, 2001).

Emerging and new DBPs

A group of 50 DBPs has been selected in base of predicted adverse health effects in the US Nationwide Occurrence Study (Weinberg *et al.*, 2002). The study covered US waters treated with the most common disinfectants (chlorine, ozone, chlorine dioxide and chloramines) and high-rich bromide waters. and included chlorinated, brominated and iodinated species of THMs; chlorinated and brominated forms of haloacetonitriles, haloketones, haloacids and halonitromethanes and chlorinated and brominated MXs. (see Table 1). Brominated DBPs were prioritized because are recognized to be much carcinogenic than their chlorinated analogues (WHO, 2000) whereas iodinated species may be more toxic than the brominated compounds according to preliminary studies (Plewa *et al.*, 2002). Particularly, brominated nitromethanes have been proved to be more cytotoxic and genotoxic than many DBPs regulated in treated water (WHO, 2000).

The analytical methodologies employed were LLE-GC/ECD, SPE-GC/MS and PT-GC/MS for halocetonitriles, halonitromethanes, iodo-THMs, haloaldeyhydes and haloketones (Krasner *et al.*, 2001; Weinberg *et al.*, 2002) and LLE-GC/ECD for haloamides and haloacetates (Onstad and Weinberg, 2001). However, several authors (Chen *et al.*, 2002; Richardson et al, 2003) when analyzed trihalonitromethanes (i.e. bromopicrin) modified the commonly used injection port temperatures and transfer line in GC/MS analysis to ≤170ºC and ≤225ºC, respectively, to avoid decomposition (i.e. bromoform) due to their thermal instability.

New halogenated DBPs are continuously discovered. Thus, the first report of a DBP having an aminoxy structure was reported by Taguchi who identified 1-aminoxy-1-chloro-butan-2-ol and 1-aminoxy-1-bromobutan-2-ol in drinking water treated with chlorine using GC/MS with low and high resolution and EI and CI modes and GC/MS/MS (Taguchi, 2001). On the other hand, the presence of an halogenated pyrrole as a DBP has been recently reported (Richardson *et al.*, 2003). This compound, 2,3,5-tribromopyrrole and other new brominated carboxylic acids were identified by GC/LRMS and GC/HRMS and EI and CI modes and 2,3,5-tribromopyrrole proved to be more cytotoxic than bromate, bromoacetic acid and MX.

MX and analogues

MX, (3-chloro-4-dichloromethyl)-5-hydroxy-2(5H)-furanone), was first identified by a Finnish group in kraft pulp mill effluents of a paper factory containing high concentration of non volatile organic matter and high free chlorine derived from the whitening process (Holmbom *et al.*, 1981). Later, MX was identified as a DBP in drinking water (Hemming *et al.*, 1986) and since then in many places around the world (Padmapriya *et al.*, 1985; Kronberg *et al.*, 1988a,b; Suzuki and Nakamishi *et al.*, 1990; Ogawa *et al.*, 1993; Romero *et al.*, 1997). Analogues of MX such as its geometrical isomer E-MX [(E)-2-chloro-4-dichloromethyl)-4-oxobutenoic acid] (Kronberg *et al.*, 1988a), oxidized and reduced MX (Kronberg *et al.*, 1988b) and brominated derivatives (BMXs) have also been identified (Suzuki and Nakamishi *et al.*, 1990; Weinberg *et al.*, 2002). The analysis of MX has traditionally been carried out by acidification prior to adsorption onto XAD-2/8 resins followed by methylation (BF$_3$/MeOH or acidic methanol) and further analysis by GC/MS (Hemming *et al.*, 1986; Suzuki and Nakamishi *et al.*, 1990; Vartiainen *et al.*, 1991; Romero *et al.*, 1997, Wright, 2002); LLE, methylation and analysis with GC/ECD (Weinberg *et al.*, 2002; Onstad and Weinberg, 2001) or high resolution MS (and Nakamishi *et al.*, 1990; Kanninganti *et al.*, 1992) has been also employed. An alternative method to HRMS used GC/ITMS/MS to determine MX and BMX in drinking water with a reported detection limit of 2 ng l^{-1} for MX and < 1 ng l^{-1} for BMXs (Zwiener *et al.*, 2001).

Other derivatizing agents such as butyl alcohol (Nawrocki *et al.*, 2001) or 2-propanol to obtain butylated or propylated derivatives of MX has proved to achieve better responses than methylation (Nawrocki *et al.*, 1997; Rantakokko *et al.*, 2004).

Table 1. High-Priority DBPs Included in Nationwide DBP Occurrence Study (Richardson, 2004)

MX and MX analogues

3-chloro-4-(dichloromethyl)-5-hydroxy-2(5*H*)-furanone (MX)
3-chloro-4-(dichloromethyl)-2-(2*H*)-furanone (red-MX)
(*E*)-2-chloro-3-(dichloromethyl)butenedioic acid (ox-MX)
(*E*)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (EMX)
2,3-dichloro-4-oxobutenoic acid (mucochloric acid)
3-chloro-4-(bromochloromethyl)-5-hydroxy-2(5*H*)-furanone (BMX-1)
3-chloro-4-(dibromomethyl)-5-hydroxy-2(5*H*)-furanone (BMX-2)
3-chloro-4-(dibromomethyl)-5-hydroxy-2(5*H*)-furanone (BMX-3)
(*E*)-2-chloro-3-(bromochloromethyl)-4-oxobutenoic acid (BEMX-1)[b]
(*E*)-2-chloro-3-(dibromomethyl)-4-oxobutenoic acid (BEMX-2)[b]
(*E*)-2-bromo-3-(dibromomethyl)-4-oxobutenoic acid (BEMX-3)[b]

halo acids
3,3-dichloropropenoic acid

halomethanes
chloromethane
bromomethane (methyl bromide)[a]
dibromomethane
bromochloromethane
bromochloriodomethane
dichloroiodomethane
dibromoiodomethane[b]
chlorodiiodomethane[b]
bromodiiodomethane[b]
iodoform[b]
chlorotribromomethane
carbon tetrachloride

halonitromethanes
bromonitromethane
chloronitromethane[b]
dibromonitromethane
dichloronitromethane[b]
bromochloronitromethane[b]
bromodichloronitromethane[b]
dibromochloronitromethane[b]
tribromonitromethane (bromopicrin)[b]

haloacetonitriles
bromoacetonitrile
chloroacetonitrile
tribromoacetonitrile
bromodichloroacetonitrile
dibromochloroacetonitrile

Halonitromethanes
bromonitromethane
1,1-dibromopropanone
1,1,3-trichloropropanone
1-bromo-1,1-dichloropropanone
1,1,1,3-tetrachloropropanone
1,1,3,3-tetrachloropropanone
1,1,3,3,-tetrabromopropanone[b]
1,1,1,3,3-pentachloropropanone
hexachlorpropanone

haloaldehydes
chloroacetaldehyde
dichloroacetaldehyde
bromochloroacetaldehyde[b]
tribromoacetaldehyde[b]

haloacetates
bromochloromethyl acetate

haloamides
monochloroacetamide[b]
monobromoacetomide[b]
dichloroacetamide
dibromoacetamide[b]
trichloroacetamide[b]

nonhalogenated aldehydes and ketones
2-hexenal
5-keto-1-hexanal[c]
cyanoformaldehyde
methyl ethyl ketone (2-butanone)[c]
6-hydroxy-2-hexanone[c]
dimethylglyoxal (2,3-butadione)

volatile organic compounds and miscellaneous DBPs
1,1,1,2-tetrabomo-2-chloroethane
1,1,2,2-tetrabomo-2-chloroethane
methyl *ter*-butyl ether[c]
benzyl chloride

[a] Not a DBP, but included because it is an important source water contaminant.
[b] DBP not originally prioritised (identified in drinking water after initial prioritisation), but included due to similarity to other priority compounds.
[c] DBP not given a high priority, but included for completeness sake to provide more representation to ozone DBPs for occurrence.

Derivatization in the GC injection port liner with BSTFA to form trimethylsilyl derivatives of MX extracts has also proved to be a suitable method for its determination (Rezemini *et al.*, 2002).

Rantakokko et al (2004) studied the matrix effects in the GC/MS determination of propylated derivatives of BMXs and concluded that the use of PTV splitless injection, a sample clean-up (tC_{18} cartridge), extraction with Oasis HLB and a frequent maintenance of the GC system are required to determine MX and BMXs at <1 ng l^{-1}. A complete review of MX and analogues is given in another chapter of this issue (Andrjezewski, 2005).

N-Nitrosodimethylamine (NDMA)

NDMA is an emerging DBP formed in drinking water and wastewater treatment with chloramines (USEPA, 1997; Choi and Valentine, 2002; Mitch *et al.*, 2003) or chlorine disinfection (Mitch *et al.*, 2002), as well as originating from point-source pollution (contaminant from rocket fuel, plasticizers, polymers, batteries, etc.). NDMA has been classified as a probable human carcinogen by the US Environmental Protection Agency (USEPA, 1997). Risk assessments from the US EPA identify a theoretical 10^{-6} lifetime risk level of cancer from NDMA exposures as 0.7 ng l^{-1} (USEPA, 1997) but it is not currently regulated in the USA for drinking water except in California that established a temporary action level of 10 ng l^{-1} for NDMA in drinking water (California Dpt. Health., 2000). At present, there is not an EPA approved analytical method for determining NDMA in drinking water at the required part-per trillion level concentration due to the small molecular size and polarity nature of NDMA.

The original analytical method was developed by the Canadian Ministry of the Environmental (MOE, 1990) which involved liquid-liquid extraction in a separatory funnel at neutral pH, using deuterated NDMA (NDMA-d_6) as an internal standard and further analysis by GC/HRMS of the extract. Liquid-liquid extraction, with NDMA-d_6 as internal standard followed by GC/MS using positive chemical ionization (PCI) with methanol or ammonia, was also used to achieve detection limits at the sub part per trillion levels of NDMA (Yoo *et al.*, 2001). Another alternative sample preparation technique was continuous liquid-liquid extraction (CLLE) under either natural or basic conditions (Eaton and Bridges, 2000) but it requires more expensive instrumentation and large volume consumption of water samples. Solid phase adsorbents were also investigated by other authors to address this problem. Munch et al (2003) employed coconut charcoal as adsorbent, dichloromethane as eluting solvent for NDMA and other nitrosamines and GC/CI-MS/MS analysis using methanol as the CI reagent to achieve NDMA limits around 1 ng l^{-1} level. Ambersorb 572 granules were used by Taguchi *et al.* (1994); NDMA was adsorbed onto the granules and then the desorbed Ambersorb was filtrated and desorbed into the autosampler vial which is a difficult procedure. Ambersorb 572 and methylene chloride as elution solvent were also used to obtain good precision, with a relative standard deviation (RSD % < 20%) and a detection limit of the method of 1 ng l^{-1} for a sample size of 500 mL (Luo *et al.*, 2003). Fields *et al.* (2004) optimized the Tagushi's method using Ambersorb 572 (200 mg), a higher extraction time (120 min.), no salt addition and no pH adjustment as a preconcentration method. The extracts were analyzed by GC/CI-MS/MS for the determination of NDMA and other related N-nitrosodialkylamines at or below 1 ng l^{-1} minimum detection levels. Cheng *et al.* (2004) examined and refined two SPE methods (Ambersorb 572 and a combination of the former adsorbent and Envi-carb cartridges) and two traditional LLE methods (manual and micro-LLE). All methods were suitable to determine NDMA to a level of 2 ng l^{-1} and other nitrosamines to a level of 2-4 ng l^{-1} in a broad range of water matrices except for micro-LLE with a reported level of 7 ng l^{-1} for NDMA and 5-12 ng l^{-1} for the other nitrosamines studied. The extracts were analyzed by GC/CI-MS/MS using methanol (for manual LLE and Ambersorb methods) or acetonitrile (for micro-LLE and Ambersorb-Envi-carb

methods) positive chemical ionization (PCI). Charrois *et al.* (2004) developed a SPE method using Ambersorb 572-Lichrolut EN and GC/MS ammonia positive chemical ionization, which favored the formation of adducts and increasing the selectivity compared to methanol PCI or LRMS-EI. The selectivity of $[M+18]^+$ and $[M+1]^+$ ions obtained in ammonia PCI mode were more distinctive for quantification compared to low mass fragments produced by EI that allowed for the detection of NDMA at the 1.6 ng l^{-1} level.

More recently, several workers have investigated the use of SPME for NDMA analysis; SPME has only so far been demonstrated to be linear above about 50 ng l^{-1} (Eaton and Bridges, 2000) and having a detection limit of 30 ng l^{-1} (Cheng *et al.*, 2004). A complete review of NDMA is given in another chapter of this issue (Andrjezewski, 2005).

Highly polar and hydrophilic DBPs and high molecular weight DBPs identification

As previously stated, it is believed that the myriad of DBPs identified until now (>500) represent less than 50% of the total organic halide (TOX) in chlorinated treated water, and the same percentage of the assimilable organic carbon (AOC) in ozonated drinking water (Stevens *et al.*, 1998; Krasner *et al.*, 1996; Richardson *et al.*, 2002b). The possibility that a major part of the unknown TOX can be attributed to highly polar or high molecular weight DBPs is feasible (Khiari *et al.*, 1996; Zhang *et al.*, 2002).

GC/MS which is the common technique used to identify DBPs is restricted to low molecular weight, volatile and semivolatile compounds but is not suitable for the identification of highly polar, hydrophilic, non volatile compounds and high molecular weight DBPs (MW>500 Da). To overcome these limitations, LC/MS or LC/MS/MS (APCI, ESI) appears to be an attractive alternative taking into account the improvements in LC/MS instrumentation that allows for the identification of compounds in the range of low µg l^{-1} to ng l^{-1} levels. However, limitations of LC/MS such as lack of library database as available for GC/MS; specific operating parameters for different analytes; ion suppression in ESI ionization due to the presence of inorganic ions commonly present in chlorinated drinking water (i.e. sodium, chloride) or ion peaks in almost every mass unit in chlorinated humic samples are among the reasons of its non routine use. Several review articles have addressed the analytical challenge of unaccounted DBPs (Weinberg, 1999; Urbansky, 2000; Richardson, 2002c; Zwiener *et al.*, 2004a,b; Zwiener and Richardson, 2005). Kopfler et al (1984) and Khiari et al (1997) used ultrafiltration membranes (UF) to isolate fractions of TOX in chlorinated and chloraminated waters. Both obtained similar results, about 33-50% of TOX had a molecular weight >500 Da; the second largest fraction of TOX (14%) was in the range of >500 and <5000 Da(10) or 30% in the range of >500 and <3000 Da in Khiari's study (1997). The highest molecular weight distribution accounted 9% of TOX (>50,000 Da) and 8% (for >10,000 Da), respectively. Zhang and Minear (2002) treated fulvic acid with ^{36}Cl-labeled chlorine to study its distribution in TOX fractions after UF and size exclusion chromatography (SEC) separation and fractionation and further analysis by LC/ESI-MS/MS. The distribution of ^{36}Cl in TOX fractions was disperse with an average molecular weight of around 2000 Da. Recent efforts to characterize the high molecular weight DBPs from chlorination of humic substances have been carried out (Zhang et al 2004,2005) by LC/ESI-MS/MS in the negative mode. They found that chlorine-containing compounds produce chloride ion fragments by MS/MS which can be used as a fingerprint for chlorinated DBPs (Zhang *et al.*, 2004) and many high molecular weight compounds were tentatively found in the UF-SEC fractions of chlorinated fulvic samples with and without coagulation pretreatment.

Inorganic anions: bromate, chlorate and chlorite

Bromate has been identified as an inorganic by-product (DBP) following ozonation (Haag and Hoigne, 1983). Health effects research indicates it to be a suspected human carcinogen which exhibits a potential 10^{-4} risk of cancer after a lifetime exposure in

drinking water at 5.0 µg l^{-1} and a potential 10^{-5} risk at 0.5 µg l^{-1} (USEPA, 1994). Other inorganic anions such as bromide, chlorite and chlorate have been produced as DBPs.

In recent years several methods have been published by EPA which specify bromate as a target analyte. Hautman and co-workers (2001) examined the capabilities and performance of these methods cited below. The limitation of available compliance monitoring methods for trace bromate was one of the factors in establishing the Stage 1 D/DBP bromate MCL at 10 µg l^{-1}. The first of these EPA methods was EPA Method 300.0, (the most recent publication of this method was revision 2.1.) (Pfaff, 1993); it was the first EPA ion chromatographic (IC) analytical method and remains widely accepted as the standard EPA IC for common ions. This method, divided into Part A for common anions and Part B for the oxyhalides, presented a bromate minimum detection limit (MDL) of 20 µg l^{-1}, too high to support a bromate MCL at 10 µg l^{-1}. EPA Method 300.1 (Hautman *et al.*, 1997) applied the basic IC principles of the method cited above but redefined the operating conditions (columns, eluent and injection volume) to enable the quantitation of significantly lower concentrations of bromate (MDL of 1.4 µg l^{-1}), even in the presence of up to 50 mg l^{-1} chloride. EPA Method 321.8 (Creed *et al.*, 1998) involves the IC separation of bromate followed by detection using inductively coupled argon plasma (ICAP) mass spectometry (MS) and has been reported as both a very selective and sensitive procedure with MDL of 0.30 µg l^{-1} (Creed *et al.*, 1996,1997). This method allows for the monitoring of the latter eluting bromide anion (Br^{-}) in the same analysis, although the bromide anion is not listed in the method's target analyst list, Recently, a new EPA Method 317 (Wagner *et al.*, 1998) has been published which improves trace bromate measurements using a postcolumn reagent, *o*-dianisidine dihydrochloride (ODA); the postcolumn absorbance detection system is connected in series, directly to the instrument configuration described in EPA Method 300.1. The MDL for this method can be 0.71 or 0.12 µg l^{-1} when suppressed conductivity or postcolumn reagent (PCR) was considered as a detection method. The elimination of the chlorite interference in this method (Wagner *et al.*, 2000) permits the analysis of trace bromate levels in all drinking water matrices. In the EPA method 326.0 (Wagner *et al.*, 2002) to facilitate the low level of detection of bromate, the suppressed effluent from the conductivity detector is combined with an acidic solution of KI containing a catalytic amount of molybdenum VI. The mixture is heated at 80ºC where the bromate reacts with iodide to form the tri-iodide which is measured by its UV absorption at 352 nm. The method is able to determine chlorite, bromate, bromide and chlorate at 2.0; 1.2; 1.7 and 1.7 µg l^{-1} levels, respectively. Snyder et al. (2004) recently reported an LC/MS/MS (negative ESI) method that uses a low-volume injection (10 µl) and sulfate/carbonate pretreatment in order to reduce interferences and improve sensitivity. The reporting limits of 0.050-0.100 µg l^{-1} for perchlorate, bromate, iodate and chlorate is achieved and was applied to bottled, tap and surface waters.

Perchlorate

Perchlorate originates as a contaminant in ground water and surface waters from the dissolution of ammonium, potassium, magnesium, or sodium salts. Sources for the contamination include chemical fertilizers and various other chemical and industrial sources. One major source of contamination is the manufacture of ammonium perchlorate for use as the oxidizer component and primary ingredient in solid propellant for rockets, missiles and fireworks. Perchlorate infiltrates the watershed through a variety of mechanisms, such as leaching and groundwater recharge; this infiltration threatens the water supplies of several regions, such as the southwestern United States (Urbansky, 1998; 2000a). Perchlorate is a health concern, as it interferes with the ability of the thyroid gland to produce thyroid hormones (Urbansky, 1998; 2000). Therefore, it has been added to the US Environmental Protection Agency's Candidate Contamination List (CCL), which is the list from which future regulated drinking water compounds will be

selected (Federal Register, 1998; USEPA, 1998a). In California, perchlorate contamination of public drinking water wells has recently been a serious problem; the Department of Health Services (DHS) established a drinking water action level for perchlorate at 18 µg l^{-1}. In 2002, California DHS revised their drinking water action level for perchlorate to 4.0 µg l^{-1} (California DHS, 2003).

Efforts to establish the extent of perchlorate contamination across the US and possibly set regulatory limits has prompted considerable interest in the development of improved methods for the analysis of low perchlorate. Ion-selective electrodes function down to around 70 µg l^{-1}, which can be improved to 10 µg l^{-1} when combined with capillary electrophoresis, which separates interfering ions from perchlorate (Hauser et al., 1994). The addition of an ion-pairing agent to the aqueous perchlorate solution and the extraction of the ion pair with an organic solvent have resulted in detection limits down to 3 µg l^{-1}. However, at this level, common ions such as nitrate can interfere into perchlorate determination (Ensafi and Rezaei, 1998; Burns and Tungkananuruk, 1987). Conventionally, the ion pair is formed with a good chromophore, such as a dye, and the perchlorate may be determined spectrophotometrically (Ensafi and Rezaei, 1998; Burns and Tungkananuruk, 1987). The use of a complexing agent for perchlorate increases selectivity but does not necessarily improve sensitivity (Urbansky et al., 1999b).

The detection of perchlorate in water is mainly concentrated on IC methods. Large, polarizable anions, such as perchlorate, are strongly retained on conventional anion-exchange columns and often display poor peak shape (Haddad and Jackson, 1990). Consequently, the analysis of perchlorate is typically performed using an hydrophilic column with an organic modifier, such as methanol or *p*-cyanophenol, added to the mobile phase to minimize adsorption and improve peak shape (California DHS, 1997a). EPA developed Method 314.0 to analyze trace levels of perchlorate in drinking water (Hautman et al., 1999) based on work that had been carried out by the State of California and Dionex® (California DHS, 1997b; Dionex, 1998). Researchers investigated application of new anion-exchange columns for the determination of trace level perchlorate using IC. Wirt and co-workers (1998) employed an IonPac AS 11 column, hydroxide eluent and suppressed conductivity with ASRS suppressor; the primary advantage of using the more hydrophilic column was that *p*-cyanophenol was not required in the eluent. Jackson et al. (1999) also discussed the suitability of the AS11; they proposed the use of a large loop injection (1000 µg l^{-1}) with a Dionex IonPac AS11 column, a 100 mM hydroxide eluent, suppressed conductivity detection and a MDL of 0.3 µg l^{-1}. One year later, they reported on the development and application of a new anion-exchange column for the determination of trace level perchlorate (Jackson et al., 2000). The IonPac AS16 column is more hydrophilic and has a significantly higher ion-exchange capacity than either the AS5 or AS11 columns. On the other hand, the AS16 column allows for the injection of higher ionic strength samples and can be used in conjunction with an automated KOH eluent generator, which eliminates the need to manually prepare eluents and increases the level of automation and ease-use of the IC system. The method is free of interferences from common inorganic anions; presented quantitative recoveries at µg l^{-1} and the MDL of 150 ng l^{-1} permits quantification of perchlorate below the levels that ensure adequate health protection. Liu et al. (2002) proposed a new method of determining trace level of bromate and perchlorate in drinking water by IC with an evaporative preconcentration technique. Due to the fact that concentrations of bromate and perchlorate in drinking water are very low and large amounts of chloride can interfere with the determination of bromate, they proposed that, prior IC analysis, the drinking water was treated with an OnGuard-Ag cartridge to remove the superfluous chloride and concentrated 20-fold using a PTFE beaker in a domestic microwave oven for 15 minutes. That allowed MDL's for bromate and perchlorate of 0.1 and 0.2 µg l^{-1}, respectively. Later, Liu and Mou (2003) determined trace levels of haloacetic acids (with

MDL's between 1.1 and 9.32 µg l^{-1}) and perchlorate (with MDL 0.60 µg l^{-1}) in drinking water by IC with direct injection. The authors tested a hydroxide-selective hydrophilic column and a gradient elution of sodium hydroxide, methanol and deionized water and then, the nine HAAs, fluoride, chloride, nitrite, nitrate as well as perchlorate could be simultaneously determined in one run within 34 minutes.

Although IC is emerging as the most viable means for the routine quantification of trace level perchlorate, this anion has been determined by ESI-MS after ion-pair extraction and by ESI-MS/MS (Magnuson et al., 2000b; Koester et al., 2003). The sensitivity of ESI-MS detection is comparable to (or greater than) conductivity detection, with some method detection limits in the sub-µg l^{-1} range. The additional capabilities of MS detection provide high detection specificity, allowing analyte confirmation and quantification of unresolved solutes. Magnuson et al. (2000b) combined ion-pair extraction with ESI-MS to determine perchlorate at trace levels in drinking water. They investigated cationic surfactants, such as alkyltrimethylammonium salts, for their dual role in the formation of a solvent extractable ion pair and electrosprayable selective complex for mass detection to achieve a MDL of 100 ng l^{-1}.

The combination of IC with MS detection is emerging as an important tool for the analysis of ionic compounds in drinking water, as it provides increased specificity and sensitivity compared to conductivity detection. Roehl and co-workers (2002) reported on application of IC/ESI-MS for the confirmation and quantitation of bromate, perchlorate, haloacetic acids and selenium species in various water samples.

Recently, Wagner *et al.* (2004) described the work at EPA's Technical Support Center to increase the sensitivity for perchlorate using EPA Method 314.0 protocols with suppressed conductivity detection. This work describes the use of 2 mm columns with a large-loop direct injection method, a column concentration technique and this concentration technique with a background reduction step, to increase the sensitivity for the analysis of trace levels of perchlorate in high ionic strength matrices. The concentrator columns studied were the Dionex TAC LP-1 and a new Dionex high capacity Cryptand concentrator column; the use of a surrogate to monitor trapping efficiency for the concentration technique and the use of confirmational columns to minimize the potential for false positives are also discussed.

To support perchlorate monitoring at low levels, EPA is currently investigating three analytical approaches that could offer enhanced sensitivity and selectivity. These techniques include LC/MS, IC/MS and the revision of the current IC based methods.

CONCLUSIONS

In spite of the tremendous effort carried out to obtain a better knowledge of the generated DBPs in treated water, there is still a long way to go. Lack of standards commercially available to accurately quantify the new DBPs or i.e. the emerging contaminants found in US Nationwide Occurrence Study is one of the problems encountered. The increasing use of instrumental techniques such as LC/MS or LC/MS/MS which are now capable of identifying compounds at the sub-µg l^{-1} level has opened a promising way to a better characterization of the TOX and AOC fractions. As examples of the usefulness of this technique, new DBPs formed by chlorination or ozonation of anthropogenic pollutants present in raw water such as halogenated derivatives of bisphenol A; alkylphenol polyethoxylates and metabolites; estrogens (i.e. ethynilestradiol, estradiol); microcystins or pharmaceuticals among other compounds have been reported.

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