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Determination of halonitromethanes in treated water

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ABSTRACT

As halonitromethanes (HNMs) have begun to play an increasingly important role as disinfection by-products, the development of a highly sensitive method for their analysis has become a priority. The mass spectrometric behavior of the 9 HNMs revealed that trihalonitromethanes are more unstable than di- or monohalonitromethanes under common chromatographic conditions. The absence of a comprehensive method for HNMs has given rise to the development of the first method for the whole array of these species, involving the selection of a solventless technique. Single drop microextraction in the headspace mode (HS-SDME) was selected as it is inexpensive and easy to operate. Comparative measurements through EPA liquid–liquid extraction (LLE) method for halogenated volatile compounds, show this approach to be superior to the manual LLE procedure (the average limits of detection (LODs) for the 9 HNMs were 0.5 and 1 μg/L for the HS-SDME and EPA methods, respectively), adequate precision (8.2 and 7.0% for HS-SDME and EPA methods, respectively) and does not consume excessive solvent since the total extract (~2 μL) was injected completely into the GC–MS instrument. The method was used to measure HNMs in treated water and the results were compared to the EPA method in parallel.

1. Introduction

Water is a scarce commodity and a fundamental resource for the human being since it plays a decisive role in health. Since the end of the XIX century, water disinfection has been used to reduce the incidence of illnesses. Chemical disinfectants (chlorine, chloramines, ozone, chlorine dioxide, etc.) are effective in killing harmful microorganisms in drinking water, but they also oxidize organic matter that forms disinfection by-products (DBPs) [1–4]. Although more than 600 DBPs have been reported in the literature, only 11 are currently regulated [1,5]. Among the unregulated DBPs, the 9 halonitromethanes (HNMs) receive special attention because of their potentially high toxicity and their occurrence in final waters at some treatment facilities [6]. Chloropicrin (trichloronitromethane, TCNM) has been the most commonly measured example in this class followed by bromonitromethane (BNM) and bromopicrin (tribromonitromethane, TBNM), which are a potential concern for toxicity [7,8]. Average concentrations in treated water containing bromide [9] have been reported between 0.1 and 10 μg/L for some HNMs and between 0.9 and 1.5 μg/L for TCNM in wastewater treatment plant effluents [10]. Despite the increasing amount of the literature on HNMs, there has been little systematic research reported on a whole array of HNM species due to the lack of commercial chemical standards in all the species, which only became available in the early 2000s. For this reason it has only recently become possible to establish the formation and speciation characteristics of HNMs as well as the factors controlling their formation in drinking waters [10–12]. In these studies, liquid–liquid extraction has been employed as a preliminary step, using the EPA methods proposed to determine halogenated volatile organic compounds (VOCs) in water [13], in order to determine some HNMs by gas chromatography–electron capture detection (GC–ECD) [9–12] or by GC mass spectrometry (MS) [14]. Other alternatives for VOCs (including TCNM) such as solid phase microextraction (SPME) with GC–MS and Purge&Trap-GC–MS [15] have also been used. Chloropicrin or TCNM (the first HNM identified as a DBP) in a mixture of other chlorine VOCs, prepared with distilled water, has been determined for headspace (HS)-SPME–GC–ECD between 0.1 and 2.5 μg/L [16] and by HS and manual injection into a GC–MS [17] or GC–ECD [18] with limits of detection (LODs) of 0.5 or 2.5 μg/L, respectively. However, these methods heat the samples in the injector at 175–250 °C, which favor up to 50% decomposition of TCNM [14]. In summary, neither have proper methodologies been developed for the 9 HNMs nor has any study of the chromatographic temperatures of the GC–MS been found to minimize/eliminate the decomposition of the 9 compounds. Only BNM and TCNM have been found in the NIST (No. 69) or Wiley spectral library database, although mass spectral ions of the 9 HNMs have been reported in the bibliography [6].

As outlined above, to date the EPA methods (for halogenated VOCs) using GC to determine some HNMs in water require liquid–liquid extraction with methyl tert-butyl ether (MTBE) which

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implies great solvent consumption and cost. To overcome such problems, recent research activities have been oriented toward the development of miniaturized sample preparation techniques like SPME [19] and liquid phase microextraction (LPME) [20–23]. In DBPs, LPME has been used for the determination of trihalomethanes (THMs) and more recently for haloacetic acids [24] but never for HNMs. In order to find precedents applying LPME methods to HNMs, we have to refer to the 4 THMs which are also volatile DBPs. Two similar methods based on single drop microextraction (SDME)–GC–ECD are proposed for the 4 THMs with similar LODs (0.2–0.4 μg/L) using 1-octanol [25] or *n*-hexane [26] as extractant. Direct hollow fiber (HF)-LPME–GC–ECD uses 25 μL of 1-octanol at 35 °C, providing LODs of 0.01–0.2 μg/L [27]. The most recent method to determine the 4 THMs by LPME–GC–MS [28] is based on the solidification of a floating organic microdrop (7 μL of 1-undecanol) with enrichment factors up to 480-fold (LODs, 0.03–0.08 μg/L), but it requires drastic extraction conditions (15 min at 60 °C) which are related to low recoveries.

Taking into consideration the foregoing, the aims of this work have been: (i) to propose the first method for the whole array of HNM species in water because 7 HNMs, although still very expensive, are now commercially available (in addition to the 2 HNMs, TCNM and BNM, that have always been on the market); (ii) to develop a solventless technique in which only one drop of an organic solvent is employed, as occurs in LPME; (iii) to avoid/minimize the decomposition of HNMs during heating in the injection port of GC and/or hot transfer line/ion source of the MS, which can complicate their identification in treated water; and (iv) to obtain enough sensitivity to determine the 9 HNMs at ng/L levels in treated water samples. The proposed HS-LPME–GC–MS method consists of a simple and fast extraction stage using a microdrop of organic solvent at the tip of a commercial microsyringe to extract the 9 HNMs from the water sample under soft conditions. The method is nearly solvent-free since the total extract was injected into the GC–MS instrument. For the first time a rigorous study has been tackled on the impact of 9 HNM decomposition in the injection port of the gas chromatograph as well as of the ion source of the mass spectrometer on the mass spectra for all 9 HNMs, since only four of them had been studied previously.

2. Experimental

2.1. Chemicals

Chloronitromethane (CNM, 90–95%), dichloronitromethane (DCNM, 95%), bromochloronitromethane (BCNM, 85–90%), bromodichloronitromethane (BDCNM, 90–95%), dibromonitromethane (DBNM, 90%), dibromochloronitromethane (DBCNM, 90–95%) and tribromonitromethane (TBNM, 90–95%) standards were supplied by Orchid Cellmark (New Westminster, Canada), while trichloronitromethane (TCNM, 99%), and bromonitromethane (BNM, 90%) were purchased from Sigma–Aldrich (Madrid, Spain) and the internal standard, fluorobenzene, from Fluka (Madrid, Spain). The solvents, 1-octanol, o-xylene, decane and 1-hexanol were purchased from Sigma–Aldrich. Ethyl acetate, methyl tert-butyl ether (MTBE) and sulfuric acid were supplied from Merck (Darmstadt, Germany). Potassium chloride, sodium chloride, anhydrous sodium sulfate, anhydrous magnesium sulfate and ammonium sulfate (dechlorinating agent) were purchased from Panreac (Barcelona, Spain). Stock standard solutions containing 1 g/L of individual halonitromethane and cumulative solutions (0.1 g/L) were prepared in ethyl acetate and stored frozen in amber glass vials at −20 °C. More dilute cumulative solutions were prepared daily in mineral water (free of DBPs) at the microgram per liter level.

2.2. Apparatus

Sample analysis was performed with a Fisons 8000 GC instrument interfaced to a Voyager mass spectrometer and controlled by a computer running MASSLAB software (Thermo, Madrid, Spain). The gas chromatographic separation was achieved on a 30 m × 0.25 mm i.d., 0.25 μm film TRB-5 capillary column coated with a stationary phase of 5%-phenyl–95%-methylpolysiloxane and supplied by Teknokroma (Barcelona, Spain). All injections were made in the split mode (1:20 split ratio) by setting the injector temperature at 170 °C. The GC oven temperature program was: 40 °C (3 min) and then raised at 40 °C/min to 140 °C (2 min) and 180 °C (3 min). The helium carrier gas (6.0 grade purity, Air Liquid, Seville, Spain) was set at 1 mL/min. The mass spectrometer was used in the following conditions: ion source temperature, 200 °C; transfer line temperature, 200 °C; electron impact ionization mode, 70 eV; scan range from *m*/*z* 30–255; time for solvent delay, 2 min. Optimization experiments were conducted in total ion chromatography (TIC) mode at 3.5 scans/s. The ions selected for identification and quantification of HNMs (SIM mode) are listed in Table 1; *m*/*z* values for fluorobenzene (IS) were: 50, 70, 96 (base peak).

2.3. Sample collection and preservation

Water samples were collected in amber glass bottles of 125 mL with poly(tetrafluoroethylene) screw caps. The bottles, containing 1.7 g of ammonium sulfate as the quenching reagent of residual chlorine [29], were completely filled to avoid evaporation of volatile compounds. To validate the sampling protocol for the analysis of HNMs, the storage time of the sample at 4 °C was studied using mineral water fortified with 5 μg/L of HNMs (except to TBNM, 10 μg/L). The studies were conducted over 10 days; the results indicated that the concentrations of CNM, DCNM, TCNM, BNM and BCNM remained constant for 7 days, whereas DCBNM, DBNM, DBCNM and TBNM only for 1 day. Thus, samples were stored at 4 °C and analyzed within 1 day of collection. For analysis, 10 mL of water sample (prepared as described below) was placed in 15 mL glass vials.

2.4. HS-SDME–GC–MS procedure

A 5 μL GC microsyringe model 87925 from Hamilton (Teknokroma, Barcelona) was used to perform the SDME experiments. Ten milliliter water samples or mineral water containing between 0.2 and 300 μg/L of each halonitromethane and 20 μg/L of fluorobenzene (IS) were placed in a 15 mL glass vial containing 3 g (2.1 mol/L) of Na_2SO_4 and the pH was adjusted at ∼3.2 by adding 30 μL of 0.1 mol/L H_2SO_4. A stirring bar (1.3 cm long) was added to the vial, which was closed immediately with a screw cap equipped with a silicon septum. Afterward the vial was stirred in a vortex mixer for 2 min in order to dissolve the salt and then placed in a water bath. A 2.5 μL volume of 1-hexanol was withdrawn into the microsyringe, the needle tip was inserted through the silicone septum and the 2.5 μL drop of extractant exposed to the headspace of the sample stirred at 600 rpm for 20 min at 30 °C. After extraction, the drop was retracted back into the microsyringe and the total extract (∼2 μL) injected into the GC instrument.

2.5. LLE procedure (EPA method 551.1)

Liquid–liquid extraction for the determination of HNMs in water was performed in triplicate following the EPA method 551.1 [13] proposed for the determination of halogenated VOCs. Samples were collected in 62 mL amber bottles with a poly(tetrafluoroethylene) screw cap containing 0.8 g of ammonium sulfate and without headspace to avoid evaporation of VOCs. A 12 mL aliquot was