



Selective and trace determination of monochloramine in river water by chemical derivatization and liquid chromatography/tandem mass spectrometry analysis



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ABSTRACT

Monochloramine (MCA) may enter the aquatic environment through three main sources: wastewater treatment plant effluents, industrial effluents and thermal power plant wastes. Up to date, there are no available data about the concentration levels of this chemical in river water due to lack of appropriate analytical methods. Therefore, sensitive and selective analytical methods for monochloramine analysis in river water are required to evaluate its environmental fate and its effects on aquatic ecosystems. Thus, in this study we describe a highly specific and sensitive method for monochloramine determination in river water. This method combines chemical derivatization of monochloramine into indophenol followed by liquid chromatography coupled to electrospray ionisation–tandem mass spectrometry (LC–ESI–MS/MS) analysis. Two precursor-to-product ion transitions were monitored (200 → 127 and 200 → 154) in positive ionisation mode, fulfilling the criteria of selectivity, in accordance with the European Legislation requirements (decision 2002/657/EC). Ion structures and fragmentation mechanisms have been proposed to explain the selected transitions. Linearity range, accuracy and precision of the method have been assessed according to the French method validation standard NF T90-210. Detecting the derivatized monochloramine (indophenol) in Multiple Reaction Monitoring (MRM) mode provided a limit of quantification of 40 ng L⁻¹ equivalent monochloramine. Applied to Loire river water (France), the developed method occasionally detected monochloramine at concentrations less than 300 ng L⁻¹, which could be explained by punctual discharges of water containing active chlorine upstream of the sampling point. Indeed, it is widely reported in the literature that the addition of chlorine to water containing ammonia (e.g., wastewater effluents and river water) may result in the instantaneous formation of monochloramine. The proposed method is a powerful tool that can be used in environmental research (e.g., assessment of environmental fate and generating of ecotoxicological data) as well as in research studies concerning the evaluation of water disinfection efficiency; but it is not currently appropriate for routine use in industrial applications given the complexity of the procedure, the instability of indophenol and the use of certain toxic reagents.

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1. Introduction

The term “inorganic chloramines” refers to a group of three chemical substances formed by a reaction between chlorine and ammonia in an aqueous medium: monochloramine (MCA, NH₂Cl), dichloramine (DCA, NHCl₂), and trichloramine (TCA, NCl₃). Concentration and speciation of these species primarily depend on two parameters: pH value and chlorine to nitrogen ratio (Cl₂/N). Only MCA has industrial uses in the water treatment sector, in

particular as a biocide for inactivating pathogenic microorganisms and viruses to prevent the propagation of water-borne infectious diseases [1–4]. Monochloramine may be also formed as unwanted by-products of water chlorination in the presence of ammonium ions (e.g. in swimming pools or polluted natural water) [5]. Compared to chlorine, monochloramine is less reactive towards the organic matter present in water and therefore produces total organic halogen and regulated disinfection by-products in lower quantities, especially trihalomethanes (THM) and haloacetic acids (AHA) [6,7]. Nevertheless, MCA has been reported to generate higher levels of nitrogenous organic halogenated by-products such as haloacetonitriles, cyanogen halides, and haloacetamides than chlorination [6,8–10]. It has also been reported that disinfection of iodide-containing waters with monochloramine or by chlorination in the presence of ammonia favours the formation of iodinated organic compounds such as iodo-THM and iodo-AHA [11–13]. In water treatment processes, monochloramine as a secondary disinfectant is currently a well-established technology and even recommended by the WHO [14]. It is used in several industrialised countries such as Canada, Japan, USA, the United Kingdom and Australia. According to estimates, around 30% of drinking water plants in the USA use MCA, and a further 8–12% intend to adopt it as a treatment [15]. In France and Germany, monochloramine is currently banned as a disinfectant for water intended for human consumption. It is, however, authorised for the disinfection of water in industrial cooling systems. It is an example used by Electricité de France (EDF) to disinfect the cooling circuits in some of its thermal power plants located alongside rivers.

Monochloramine may enter the aquatic environment through three main sources: wastewater treatment plant effluent, industrial effluent and thermal power plant waste. There is therefore a need to investigate whether the aquatic ecosystem is being affected by effluents containing residual MCA. A report on Canadian environmental quality standards for chlorine species was published in 1999 and lists the main ecotoxicological effects of MCA [16]. The lowest acute toxicity values given in this report are between 14 and 82 $\mu\text{g L}^{-1}$ for fish, and between 16 and 78 $\mu\text{g L}^{-1}$ for invertebrates. Thus, in order to assess monochloramine impact on the aquatic environment, there is a need for a sensitive and specific analytical method to quantify this compound at trace concentrations in river water.

Quantifying trace levels of inorganic chloramines poses a major challenge, since the available analytical methods, including standardised and benchmark methods, are not sensitive and specific enough to detect these compounds in river water. Scientific articles report the use of two types of methods: those involving colorimetric, titrimetric or amperometric analysis, and those involving chromatography and membrane introduction mass spectrometry (MIMS) [17]. DPD (N,N-diethyl-phenylenediamine) colorimetry is currently the most widely used method. This standardised method (EN ISO 7393) is easy to use and suitable for field measurements, but has two main limitations: its lack of MCA specificity and insufficient sensitivity ($\text{LOQ} > 30 \mu\text{g eq. Cl}_2 \text{ L}^{-1}$) for the concentrations expected to be found in river water ($< 1 \mu\text{g eq. Cl}_2 \text{ L}^{-1}$) [18]. To overcome the lack of specificity of DPD colorimetry, other colorimetric methods using the Berthelot reaction have been developed. They are based on the principle of measuring the intensity of the indophenol colour produced when monochloramine and phenol react in an alkaline medium and in the presence of a catalyst. Due to the toxic and noxious nature of phenol, several compounds are now being used as alternatives. Although specific, these methods are not sensitive enough to measure trace levels of monochloramine ($\text{LOQ} > 50 \mu\text{g eq. Cl}_2 \text{ L}^{-1}$). DPD and ferrous ammonium sulphate (FAS) titration is another standardised method routinely used by water processing laboratories. However, it is unsuitable for field use and its performance is

similar to that of DPD colorimetric testing. Amperometric titration with sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) or phenylarsine oxide (PAO, $\text{C}_6\text{H}_5\text{AsO}$) is also a widely used standardised method, especially for the *in situ* quantification of free and combined chlorine. This method's limit of quantification is similar to that of titrimetric and colorimetric methods, but it has better selectivity. Liquid chromatography (LC) and membrane introduction mass spectrometry (MIMS) methods have been developed to overcome the limitations posed by these traditional methods. Very few methods employing liquid chromatography without prior chemical derivatization of the chloramines have been developed. The detection is performed using UV photometry or electrochemical detection, which vastly reduces the sensitivity and selectivity of the measurements. In order to improve the sensitivity and selectivity, two pre-column derivatization agents have been suggested: 5-(dimethylamino) naphthalene-1-sulphonic acid (or dansyl sulphonic acid, DANSO_2H) and 2-mercapto-benzothiazole (2-MBTZ). However the reactions involving those two reagents present various limitations in terms of complexity, reaction duration and/or low yield [19,20]. Membrane introduction mass spectrometry (MIMS) was used to analyse inorganic chloramines for the first time by Kotiaho et al. [21]. The principle of this technique is a selective introduction of molecules through a membrane placed between the sample and the ion source of a mass spectrometer. MIMS has the advantage of being selective and compatible with on-line and real-time analyses without any prior sample preparation stage [22]. However, the hydrophobic nature of the membrane promotes the diffusion of apolar molecules and limits that of polar and semi-polar compounds. This discrimination is a major limitation of the method for analysing monochloramine, since the best limit of quantification obtained to date is 0.2 mg L^{-1} [23,24].

Therefore, due to the lack of sensitive and specific analytical methods, there are no quantified data on the monochloramine concentration levels in river water. Liquid chromatography coupled with mass spectrometry (LC-MS) is a highly sensitive and specific technique for the quantification of polar and semi-polar molecules at trace concentrations. However, up to date, this technique has not been tested as a potential method for monochloramine analysis, probably due to its low molar mass (51.5 g mol^{-1}). We report on the first attempts to develop a measurement method based on a combination of chemical derivatization of monochloramine into indophenol and LC-MS/MS quantification of the later. This analytical method was assessed in river water according to the French standard NF T90-210 and successfully used to measure the concentration levels of monochloramine in the water of the river Loire (France) within the framework of research activities.

2. Materials and methods

2.1. Reagents and standard solutions

2.1.1. Reagents and solvents

All reagents and solvents used to produce and analyse monochloramine were of analytical quality. Acetonitrile (HPLC grade) and potassium iodide were obtained from Scarlau (Spain) and Carl Roth (Karlsruhe, Germany) respectively. Ammonium chloride (purity $> 99.5\%$), sodium hypochlorite (15% Cl_2), sulphuric acid (purity $> 95.0\%$), N,N-diethyl-p-phenylenediamine (DPD, purity $> 99.0\%$), lithium citrate tribasic tetrahydrate (purity $> 99.0\%$) and ammonium formate (purity $> 99.9\%$) were purchased from Sigma-Aldrich (Steinheim, Germany). Monopotassium phosphate (purity $> 99.5\%$), disodium hydrogen phosphate dehydrate (purity $> 99.5\%$), ethylenediaminetetraacetic acid (EDTA, purity $> 99.0\%$), potassium iodate (purity $> 99.0\%$),

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