



Selective and sensitive method based on capillary liquid chromatography with in-tube solid phase microextraction for determination of monochloramine in water



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ABSTRACT

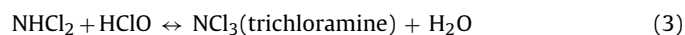
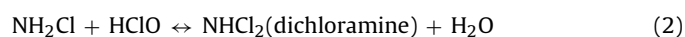
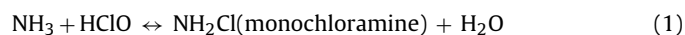
Due to the difficulties of working with chloramines, a critical examination of monochloramine standard preparation has been performed in order to select the best synthesis conditions. The analyte has been determined by in-tube solid phase extraction coupled to capillary liquid chromatography with UV detection (IT-SPME Capillary LC DAD). Potential factors affecting the response of monochloramine such as the pH of mobile phase and the volume of sample processed by IT-SPME Capillary LC DAD have been investigated and optimized. According to the results of the study, 0.1 mL or 4.0 mL of sample at neutral pH were loaded in the chromatographic system. A sensitive and selective method has been developed for the determination of monochloramine in water. Validation of the method has been performed. The linear range was 0.09–5 mg/L with linear regression coefficients (R^2) greater than 0.995. Method reproducibility expressed as relative standard deviation (RSD, %), was lower than 15%. The limits of detection (LODs) were 0.029 and 0.01 mg/L by processing 0.100 mL or 4 mL of the samples, respectively, being below the maximum residues levels allowed for this compound. The sensitivity achieved by the developed method was better than that obtained by the reference method. The developed method was applied to water samples (tap and swimming pool water).

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1. Introduction

Chloramines are nitrogen compounds with one, two or three chlorine atoms attached to a nitrogen atom [1]. Monochloramine is a weak disinfectant and a stable oxidant, so it can be used as a secondary disinfectant [2–4], while dichloramine and trichloramine are considered by-products [2] obtained after chlorine based treatment [3–8].

In aqueous solutions inorganic chloramines are formed according to the equations described below [3,5,8,10]:



The concentration of these chloramines depends on the pH, temperature and chlorine-to-nitrogen ratio [8,10,11]. The optimal pH

for monochloramine formation lies within the range 7.5–9 (the rate of its formation reaction reach the maximum at pH 8.3) and Cl/N mass ratio of 3:1–5:1 [2]. NHCl_2 presents its maximum kinetic at pH around 4.5, and at lower pHs only NCl_3 is formed. Under normal environmental conditions of pH (between 7 and 8) and 20 °C temperature, monochloramine is the predominant chloramine and it is relatively persistent, with half lives of 0.4–17.5 days in river water, and 2–9 days in drinking water [2,4]. However, for high chlorine-to-nitrogen ratios, breakpoint process takes place, which consists of chloramines and ammonia oxidation [7,10].

The study of chloramines is problematic because there are not standard solutions of inorganic chloramines commercially available, so they have to be prepared in aqueous solution and standardized by analytical methods [2]. The chloramine synthesis has strong dependence on the experimental conditions, so the concentrations obtained might vary depending on the reaction conditions.

Some of the methods proposed for the determination of NH_2Cl are standard analytical methods available to quantify chloramines and free chlorine [8]. Table 1 summarizes the main analytical properties of the methods proposed in the literature to determine monochloramine. Usually, most of these methods suffer from a lack

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Table 1
Main analytical properties of different analytical methods proposed for monochloramine in the bibliography.

Analysis method	Interferences	Pre-treatment	LOD	Ref.
Iodometric I	Oxidizing and reducing agents	Redox reaction with reagent	0.040 mg Cl ₂ /L 1 mg/L cannot be determined accurately	[23]
Iodometric II	Oxidizing and reducing agents, organic chloramines and metals.	–	–	[23]
Low-Level Amperometric Titration	Nitrogen trichloride, chlorine dioxide, organic chloramines, or halogens.	–	0.010 mg Cl ₂ /L	[23]
DPD Ferrous Titrimetric	Oxidized manganese	Redox reaction with reagent	0.018 mg Cl ₂ /L	[23]
DPD Colorimetric Method	Sample colour and turbidity, organic contaminants, oxidizing agents	Redox reaction with reagent	0.025 mg Cl ₂ /L	[24]
Syringaldazine (FACTS)	Interferences common to other methods do not affect the FACTS procedure	Redox reaction with reagent	0.1 mg Cl ₂ /L	[23]
Iodometric Electrode	Oxidizing agents	–	–	[23]
Monochlor F (Indophenol reaction)	–	Derivatization	0.27 mg Cl ₂ /L	[20]
Salicylate-spectrophotometry	Aniline	Derivatization	–	[8]
HPLC without chemical derivatization	–	–	0.08–0.43 mg Cl ₂ /L	[11][22]
HPLC with pre-column derivatization	–	Derivatization	0.33 mg Cl ₂ /L	[12,14]
HPLC with post-column derivatization	–	Redox reaction	7.1 mg Cl ₂ /L	[15]
Gas Chromatography	–	Derivatization	0.001 mg Cl ₂ /L	[16]
MIMS	–	–	0.1 mg Cl ₂ /L	[9]

of specificity because many compounds, like organic chloramines, free halogens or oxidizing and reducing agents, can modify the result of the analysis and provide false positive signals [2,8,9]. To solve this problem, more specific methods based on techniques that use physicochemical properties of the analytes, have been developed. By using HPLC, the different compounds can be separated and detected using the natural properties (redox or absorption) of the chloramines, or after a pre- or post-column derivatization. Hilin Ge et al. [11] performed an HPLC procedure for the determination of trace amounts of chloramines and compared UV photometry and electrochemistry detection. Reagents such as 5-(dimethylamino)-naphthalene-1-sulfinic acid [12], sodium benzenesulfonate [13] and 2-mercapto-benzothiazole [14] have been proposed for pre-column derivatization. KI is to date the only chemical reagent used for post-column derivatization in HPLC analysis. The resulting triiodide ions (I₃⁻) are electrochemically detected or by spectrophotometry [15]. Gas chromatography (GC) has been used to determine trichloramine in drinking water using a quadrupole MS operating in selected-ion monitoring (SIM) mode, but this study did not include monochloramine [16]. To make it suitable for GC analysis, monochloramine must be transformed into a volatile derivative by a prior chemical derivatization. Thereby, these methods are complex, time consuming and subject to the risk of sample contamination or monochloramine losses [17,18]. Finally, membrane introduction MS allows the detection and quantitation of inorganic chloramines in water samples without prior sample treatment [9,19].

Concerning to NH₂Cl (Table 1), some procedures have been established for the direct determination of NH₂Cl based on the Berthelot's method [20].

After a revision of the proposed methods for NH₂Cl determination, it can be concluded that this determination presents certain limitations, which are the lack of agreement between different authors for the synthesis of monochloramine and, in many cases, the lack of selectivity of the used procedures for its determination.

The conditions proposed for the synthesis (Table 2) can affect the concentration of the chloramine in the initial solution and also its stability.

Considering these aspects, the main objectives of this study were, (i) to review and to perform a critical examination of monochloramine standard preparation method, and (ii) to develop a rapid and simple procedure to improve the sensitivity and selectivity. In order to achieve these goals, IT-SPME Capillary LC procedure has been developed. IT-SPME allows the preconcentration of the sample and, coupled with capillary chromatographic systems, improves the sensitivity. By using this approach, the analytes do not require derivatization nor any other treatment prior to analysis, and samples can be directly injected in the equipment. Finally, the proposed procedure has been applied to determine NH₂Cl in real water samples (tap and swimming pool water). This methodology provides high speed analysis with low solvent consumption and waste generation [21].

2. Experimental

2.1. Reagents and standard solutions

All reagents used in this study were of analytical grade. Nanopure water obtained using Nanopure II system (Barnstead, USA) was used for preparation and dilution of all solutions.

Ammonium stock standard solution was prepared from ammonium chloride (Probus, Barcelona, Spain).

Sodium hypochlorite solution was obtained by diluting commercially available NaOCl solution (Scharlau, Barcelona, Spain). Methanol was of HPLC grade (Romil-SpS super purity Solvent, Cambridge, UK). Potassium iodate, sodium oxalate and orthophosphoric acid were obtained from Panreac (Barcelona, Spain). Potassium permanganate, nitroprusside and sodium hydrogencarbonate were obtained from Probus (Barcelona, Spain). Sulphuric acid was purchased from Fluka Chemike (Buchs, Switzerland).

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