



Rapid analysis of perchlorate, chlorate and bromate ions in concentrated sodium hypochlorite solutions

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ABSTRACT

A sensitive, rapid, and rugged liquid chromatography with tandem mass spectrometry (LC–MS/MS) method for measuring concentrations of perchlorate, chlorate, and bromate ions in concentrated sodium hypochlorite solutions is presented. The LC–MS/MS method offers a practical quantitation limit (PQL) of $0.05 \mu\text{g L}^{-1}$ for ClO_4^- , $0.2 \mu\text{g L}^{-1}$ for BrO_3^- , and $0.7 \mu\text{g L}^{-1}$ for ClO_3^- and a sample analysis time of only 10 min. Additionally, an iodometric titration technique was compared with the LC–MS/MS method for measurement of chlorate ion at high concentration. The LC–MS/MS method was the most reproducible for chlorate concentrations below 0.025 M while the iodometric titration method employed was the most reproducible above 0.025 M. By using both methods, concentrations of chlorate can be measured over a wide range, from $0.7 \mu\text{g L}^{-1}$ to 210g L^{-1} in hypochlorite ion solutions. Seven quenching agents were also evaluated for their ability to neutralize hypochlorite ion, thereby stopping formation of perchlorate ion in solution, without adversely impacting the other oxyhalide ions. Malonic acid was chosen as the quenching agent of choice, meeting all evaluation criteria outlined in this manuscript.

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1. Introduction

In light of anticipated heightened security requirements by Department of Homeland Security for the use of chlorine gas, water utilities may consider the use of sodium hypochlorite, as an alternative to disinfect and maintain a residual level of disinfectant in drinking water and waste water treatment applications [1]. Several regulated contaminants are present in hypochlorite ion solutions including bromate, hypochlorite itself, and chlorite ions in addition to currently unregulated oxyhalides such as chlorate ion [2–5]. Perchlorate ion is an endocrine disrupting compound that targets the thyroid in humans [6], has been recently identified as a contaminant of concern in sodium hypochlorite solutions and has been shown to increase during storage [2,7]. Interestingly, high concentrations of perchlorate ion in stored sodium hypochlorite

solutions were also correlated to high concentrations of chlorate ion [2], though the factors impacting the rate of formation are not well understood at this time. Due to the increasing concern over perchlorate ion contamination of drinking water and the need to investigate factors impacting the formation of perchlorate ion in hypochlorite ion solutions, a sensitive, precise, and rapid method for the analysis of perchlorate ion and other contaminants of concern in hypochlorite ion solutions is of utmost importance to the scientific community.

Mass spectrometry (MS) has been applied for the detection of oxyhalide anions, most commonly in conjunction with ion-chromatography (IC–MS) or liquid chromatography (LC–MS) [8–15]. US EPA method 331.0 uses LC with tandem mass spectrometry (LC–MS/MS) while US EPA method 332.0 uses IC–MS/MS to detect perchlorate ion in water. However, neither were developed to identify and quantify other oxyhalide ions at the same time [16,17].

Measurement of perchlorate and other oxyhalides, such as chlorate and bromate in concentrated sodium hypochlorite solutions, presents several challenges to the analytical chemist: sodium hypochlorite solutions are corrosive and of high salinity. The concentration differences between hypochlorite ion and other ions of interest can differ by several orders of magnitude, thus requiring

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multiple dilutions and/or multiple methods for the determination of each analyte. Chloride, sulfate, and phosphate ions have been shown to cause potential interference when measuring perchlorate ion in water [15], which may further necessitate higher dilutions or sample clean-up steps. Thus, in order to overcome potential matrix effects and possible ionization suppression, low method detection limits are necessary in order to account for the high sample dilutions. The quantitation of other co-occurring contaminants in sodium hypochlorite, such as bromate and chlorate ions [2], must also be validated.

It has been recently demonstrated that LC–MS/MS can be used to accurately measure perchlorate ion together with bromate, chlorate, and iodate ions in a variety of sample matrices, such as bottled water [18] and food supplements [19]. However these methods are generally time-consuming and have not been validated for analysis of concentrated sodium hypochlorite solutions. Electrochemical techniques have been validated for measuring chlorate, chlorite, and hypochlorite ions, in water and sodium hypochlorite solutions by amperometric titration [20] and direct potentiometric titration [21]. The iodometric titration method was chosen as a reference method for measuring the concentration of chlorate ion in concentrated sodium hypochlorite solutions. Direct potentiometric titration with sulfite ion was chosen for highly accurate and selective quantitation of hypochlorite ion.

The objective of this study was to optimize and validate an existing LC–MS/MS method [18,19] for the simultaneous identification and quantification of perchlorate, bromate, and chlorate ions in concentrated hypochlorite ion solutions. Because the new method was to be used in a subsequent investigation into the kinetics of perchlorate and other oxyhalide ions formation in hypochlorite ion solutions, a robust, and accurate method was required. Thus, an additional objective was to compare LC–MS/MS methods to other validated methods, such as iodometric titration, to identify concentration ranges at which the methods provided the most reliable results for analysis of chlorate ion. Lastly, the selection of a hypochlorite ion quenching agent for sample preservation was needed, and any effects on analysis investigated.

2. Experimental

2.1. Chemicals

Perchlorate and chlorate ions standards (>99.5% purity) were obtained from Ultra Scientific (North Kingstown, RI) and J.T. Baker (Phillipsburg, NJ), respectively. Bromate ion standard was obtained from Ultra Scientific (North Kingstown, RI). The stable-isotope labeled perchlorate ($\text{Cl}^{18}\text{O}_4^-$) and bromate ($\text{Br}^{18}\text{O}_3^-$) ions, used as internal standards, were obtained from Icon Isotopes (Summit, NJ). Trace analysis grade methanol was obtained from Burdick and Jackson (Muskegon, MI). Formic acid (1 mL ampoules, >99%) was purchased from Thermo Scientific (Rockford, IL). Hydrochloric acid (ACS reagent, 37%) was obtained from Sigma–Aldrich (St. Louis, MO) and Fisher Scientific (Pittsburg, PA). Potassium iodate (99.4–100.4% ACS Reagent) was obtained from Alfa Aesar (Ward Hill, MA). Potassium Iodide (99%) was obtained from Sigma Aldrich and Alfa Aesar (Ward Hill, MA). Sodium sulfite (98%, ACS Reagent) was obtained from Acros Organics USA (Morris Plains, NJ) and Sigma–Aldrich (St. Louis, MO). Sodium thiosulfate (99%, ACS reagent grade) obtained from Sigma–Aldrich (St. Louis, MO). Sodium chlorate, ACS Grade, $\geq 99\%$ pure bought from VWR (Brisbane, CA) was used to spike sodium hypochlorite solutions. Standard and sample dilutions were done using deionized reagent water purified by Milli-Q Gradient System (Millipore, Billerica, MA).

2.2. LC–MS/MS analysis

Tandem mass spectrometry was performed using an API4000 triple–quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) equipped with an electrospray ionization source and operated in negative ion mode. The following precursor/product ion transitions were used: $^{35}\text{ClO}_4^-$ (m/z 99) to $^{35}\text{ClO}_3^-$ (m/z 83) for perchlorate; $^{35}\text{ClO}_3^-$ (m/z 83) to $^{35}\text{ClO}_2^-$ (m/z 67) for chlorate; and $^{79}\text{BrO}_3^-$ (m/z 127) to $^{79}\text{BrO}_2^-$ (m/z 111) for bromate. The following confirmation transitions were used: $^{37}\text{ClO}_4^-$ (m/z 101) to $^{37}\text{ClO}_3^-$ (m/z 85) for perchlorate; $^{37}\text{ClO}_3^-$ (m/z 85) to $^{37}\text{ClO}_2^-$ (m/z 69) for chlorate; and $^{81}\text{BrO}_3^-$ (m/z 129) to $^{81}\text{BrO}_2^-$ (m/z 113) for bromate. Perchlorate and bromate were quantified using isotope dilution. Stable-isotope labeled versions of perchlorate ($^{35}\text{Cl}^{18}\text{O}_4$) and bromate ($^{79}\text{Br}^{18}\text{O}_4$) were used. As no source of oxygen-18 labeled chlorate was commercially available, chlorate was quantified using external calibration.

The analytes were separated using a 75×4.6 mm Synergi Max-RP C12 column with a $4 \mu\text{m}$ pore size (Phenomenex, Torrance, CA). An injection volume of $20 \mu\text{L}$ was used for all samples. A binary gradient consisting of 0.1% formic acid (v/v) in water (A) and 100% methanol (B) at a flow rate of $700 \mu\text{L min}^{-1}$ was used. The gradient was as follows: 2% B held for 1 min, increased linearly to 15% B by 2 min, changed to 95% B and held for 4 min, and finally changed to 2% B and held for 3 min. A 1 min equilibration step at 2% B was used at the beginning of each run to bring the total run time per sample to 10 min. With the use of a shorter column the analysis time was reduced to half of the original method [18,19] with all three analytes eluting after 2 min. The effects of faster separation on method performance were further investigated.

2.3. Titration method for hypochlorite, chlorite, and chlorate analysis

Potentiometric titrations with sulfite [21] were carried out using a VIT 90 Video Titrator with a P101 platinum k401 SCE electrode pair (Radiometer, Copenhagen, Denmark). Colorimetric titrations of iodine with thiosulfate were performed with a standard 50 mL laboratory glass burette to a colorless end-point. Concentrated hydrochloric acid and the sample solution were purged with nitrogen gas to minimize oxidation of iodide by oxygen prior to chlorate determination. Potassium iodate standard (0.1 M) was prepared weekly using high purity (>99.4%) potassium iodate and used to standardize sulfite and thiosulfate solutions daily. Standardization by this method resulted in standard deviations of less than three parts per thousand and less than 1% relative standard deviation. The 0.2 M SO_3^{2-} solutions were prepared from ACS reagent grade sodium sulfite. The 0.1 M $\text{S}_2\text{O}_3^{2-}$ solutions were prepared from ACS reagent grade sodium thiosulfate.

Specific conductance measurements were performed using a HACH Ion-Series Conductivity/Total Dissolved Solids meter (Hach Company, Loveland, CO).

3. Results and discussion

3.1. Validation of LC–MS/MS method for the analysis of hypochlorite solutions

The sodium hypochlorite solutions subjected for analysis ranged from 0.35% to 13%, as active chlorine, with specific conductance ranging from 51.8 to 498 mS cm^{-1} . Given high salinity and corrosiveness of these samples, and possible ionization suppression, low method detection limits (MDL) are necessary in order to account for high sample dilutions. Using the optimized separation method, standards containing 0.02, 0.1, and $0.5 \mu\text{g L}^{-1}$

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