Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies. 2023;18(3):254–264

ANALYTICAL METHODS IN CHEMISTRY AND CHEMICAL TECHNOLOGY

АНАЛИТИЧЕСКИЕ МЕТОДЫ В ХИМИИ И ХИМИЧЕСКОЙ ТЕХНОЛОГИИ

ISSN 2686-7575 (Online)
https://doi.org/10.32362/2410-6593-2023-18-3-254-264
UDC 543.621

RESEARCH ARTICLE

Determination of chlorine-containing compounds in disinfectants using ion-exchange chromatography

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Abstract

Objectives. *To develop a method for the determination of hypochlorite, chloride, chlorite, chlorate, and perchlorate ions in solution; to determine the limits of detection and quantitation for* ClO^-, Cl^-, ClO_2^-, ClO_3^-, *and* ClO_4^- *ions; to evaluate the applicability of the developed method and its suitability for disinfectant analysis.*
Methods. *Ionic chromatography using a conductometric detection system in isocratic elution mode.*
Results. *The method developed for chromatographic determination of chlorine-containing ions can be used to quantify the content of hypochlorite, chloride, chlorite, chlorate, and perchlorate ions. In isocratic elution mode at 7.5 mM NaOH and a flow rate of 0.4 mL/min, the content of chlorine-containing ions can be determined with high sensitivity. The presented method does not require the use of expensive equipment for the ultrasensitive analysis of the studied compounds.*

Conclusions. *A novel method for the simultaneous determination of hypochlorite, chloride, chlorite, chlorate, and perchlorate ions in case of their combined presence is proposed. The technique can be used to carry out routine control of the content of these disinfectant components during use, increasing their effectiveness at the same time as managing associated toxicological risks.*

Keywords: *hypochlorite ion, chloride ion, chlorite ion, chlorate ion, perchlorate ion, ionic chromatography, disinfectants*

For citation: Lapina E.A., Zverev S.A., Andreev S.V., Sakharov K.A. Determination of chlorine-containing compounds in disinfectants using ion-exchange chromatography. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2023;18(3):254–264 (Russ., Eng.). https://doi.org/10.32362/2410-6593-2023-18-3-254-264

НАУЧНАЯ СТАТЬЯ

Определение хлорсодержащих соединений в дезинфицирующих средствах с использованием ионообменной хроматографии

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Аннотация

Цели. *Разработать методику определения гипохлорит-, хлорид-, хлорит-, хлорат- и перхлорат-ионов при их совместном присутствии в дезинфицирующих средствах. Определить пределы обнаружения и пределы количественного определения ионов* ClO^-, Cl^-, ClO_2^-, ClO_3^-, ClO_4^-. *Провести расчеты валидационных параметров разработанной методики, а также оценить ее пригодность для анализа дезинфицирующих средств.*
Методы. *Ионообменная хроматография с системой кондуктометрического детектирования в изократическом режиме элюирования.*
Результаты. *Новая методика хроматографического определения хлорсодержащих ионов позволяет количественно оценить содержание гипохлорит-, хлорид-, хлорит-, хлорат- и перхлорат-ионов при их одновременном нахождении в модельном растворе и в дезинфицирующих средствах. Изократический режим элюирования 7.5 мМ NaOH при скорости движения потока 0.4 мл/мин позволяет с высокой чувствительностью определять ионы, содержащие атом хлора. Разработанная методика не требует использования дорогостоящего оборудования, необходимого для сверхчувствительного анализа исследуемых соединений.*

Выводы. *Впервые предложена методика определения гипохлорит-, хлорид-, хлорит-, хлорат- и перхлорат-ионов при совместном присутствии. Ожидается, что разработанная методика позволит проводить рутинный контроль содержания этих компонентов в дезинфицирующих средствах при их практическом использовании, что приведет к повышению эффективности применения дезинфектантов на их основе и снижению возможных токсикологических рисков.*

Ключевые слова: *гипохлорит-ионы, хлорид-ионы, хлорит-ионы, хлорат-ионы, перхлорат-ионы, ионообменная хроматография, дезинфицирующие средства*

Для цитирования: Лапина Е.А., Зверев С.А., Андреев С.В., Сахаров К.А. Определение хлорсодержащих соединений в дезинфицирующих средствах с использованием ионообменной хроматографии. *Тонкие химические технологии.* 2023;18(3):254–264. https://doi.org/10.32362/2410-6593-2023-18-3-254-264

INTRODUCTION

One of the key roles in public health consists in preventing the transmission of infectious diseases. The main basis of non-specific prophylaxis consists in implementing disinfection measures using appropriate means. Nowadays, many food products undergo thorough disinfection treatment during the preparation of goods for sale [1–3], typically involving the use of chlorine-containing disinfectants. Since, due to its high toxicity, pure chlorine is not suitable for these purposes, various chlorine-containing compounds—e.g., sodium hypochlorite—are used [2, 4–7]. The industrial production of sodium hypochlorite involves the electrolytic dissociation of an aqueous solution of sodium chloride. In the process, byproducts containing chlorite, chlorate, and perchlorate ions can also be formed [3, 8]. In an aqueous medium, due to being in chemical equilibrium, such ions can transform into different forms [9].

Chlorine-containing anions pose a particular risk to human health [3, 10]. For example, perchlorate ions have a negative effect on the production of thyroid hormone, which affects the functioning of the brain. The US Environmental Protection Agency has set the maximum allowable concentration of such substances at 15 µg/L, while the maximum pollution limit is set at 2 µg/L [11]. The World Health Organization, which is responsible for controlling the content of chlorate ions in drinking water, sets its maximum permissible concentration at 0.7 mg/L [12]. Since disinfectants based on chlorine compounds are typically used in food production processes, their residual amounts are found in dairy products, vegetables, and drinking water [1, 2, 10, 13–16].

Classical methods for the determination of chlorine-containing compounds in various objects are iodometric and potentiometric titration, colorimetric and fluorometric methods, capillary electrophoresis, etc. [4, 6, 12, 17–19]. Contemporary approaches are based on the use of ultrasensitive sensors to chloride-containing ions, which use elements of the platinum and palladium series in tandem with spectrophotometry, as well as on high-performance liquid chromatography methods using a mass-selective detection system [5, 7, 11, 20, 21]. Although such methods offer high sensitivity and a low detection limit of the studied compounds, they remain expensive.

Ion-exchange chromatography has been used in the analysis of chlorine-containing compounds since the end of the 20th century [22]. The first studies with chromatographic separation of chlorate and chlorite ions were carried out under conditions of low pH values. However, this solution led to the degradation of other compounds in the analyzed solution. Subsequent methods for analyzing the content of chlorine-containing ions in drinking water and other inorganic objects are based on the use of weakly alkaline or weakly acidic eluents to achieve a better separation of the compounds under study [16, 23].

Contemporary analysis techniques are based on a similar class of eluents [24, 25]. For example, depending on the type of analytical column for the analysis of chlorine-containing ions, eluents can be based on orthophthalic acid and acetonitrile. Eluents based on sodium carbonate and bicarbonate (also separately) and alkaline eluents based on sodium or potassium hydroxide in various concentrations are also used. In order to improve existing ion exchange chromatography methods, high resolution mass-selective detection systems are used in place of classical conductometric detection. This makes it possible to increase the analysis sensitivity and suppress the effect of high concentrations of side ions [26–28].

An analysis of the literature data shows that works based on the quantitative assessment of chlorine-containing ions fail to present a general picture of the analysis of all such ions simultaneously. Most studies in this area are aimed at studying ions having dangerous effects on human health: chlorite, chlorate, and perchlorate ions [24, 28]. At the same time, the complexity of chromatographic analysis involves a large number of "interfering" ions, for example, Cl^-, whose chromatographic peaks, due to high concentrations, overlap the signals of other compounds [13].

Thus, the present study sets out to develop a method for determining hypochlorite, chloride, chlorite, chlorate, and perchlorate ions in their combined presence in solution using ion exchange chromatography with a conductometric detection system. The improved approach can be used to carry out quality control of manufactured disinfectants and other possible objects without the use of expensive equipment. The technique can additionally be used to determine the studied compounds even in trace amounts, thus reducing possible toxicological risks.

MATERIALS AND METHODS

Reagents

The study used sodium chlorite (80%), potassium chlorate (99%), potassium perchlorate (99.9%), and sodium hypochlorite solution having a base substance content of 10%, manufactured by *Sigma-Aldrich* (USA). Sodium hydroxide (99.3%) was produced by *VWR* (USA). Potassium permanganate, hydrochloric acid, iodine, sodium thiosulfate, potassium bromide, sodium carbonate, sodium bicarbonate, and potassium biphthalate used in the work were of analytical grade or higher and used without further purification.

Samples of disinfectants

In order to assess the suitability of the developed method, three commercially available samples of disinfectants—anolytes were studied. In order to maintain experimental independence, the samples were submitted for testing after removing information about the manufacturer and component composition of the studied products from the packaging.

Equipment

The following equipment was used in the work: Elmasonic S 70 H ultrasonic bath (*Elm*a, Germany); EBA 280 centrifuge (*Hettich*, Germany); Millipore Direct Q3 water purification system (*Millipore*, USA); Adventure AR-2140 balance with a resolution of 0.0001 g (*Ohaus*, Switzerland); variable volume dispensers (*Sartorius*, Germany).

Preparation of solutions

For the preparation of eluents and solutions of the studied compounds, degassed deionized water was used. Degassing was carried out for 15–20 min at a temperature of 50°C using an ultrasonic bath with an ultrasound frequency of 37 kHz. The preparation of eluent solutions was carried out by weighing the required amount of the substance to an accuracy of four decimal places and diluting it in prepared water. The preparation of solutions of chlorine-containing compounds used to develop calibration curves was carried out by diluting the stock solution of compounds. The stock solution was prepared by weighing the required amount of the substance to an accuracy of four decimal places and diluting it in prepared water.

Synthesis of sodium hypochlorite

Sodium hypochlorite was synthesized by gradual addition of crystalline potassium permanganate (0.025 mol) to concentrated hydrochloric acid (0.20 mol; 4 M) with heating. Gaseous chlorine (0.063 mol) released as a result of the reaction was introduced into a sodium hydroxide solution (0.13 mol; 45 wt %) until the end of gas evolution. The resulting solution was filtered, cooled to 15°C, and centrifuged at 5000 rpm. The formed precipitate was separated by decantation and dried under vacuum for 24 h in a dark place. The content of sodium hypochlorite in the product confirmed by iodometric titration was 39.8 wt %.

Infrared (IR) spectroscopy

The IR spectra of sodium hypochlorite hydrate, potassium chlorate, and sodium chloride were recorded on an InfraLYUM FT-08 IR-Fourier spectrometer (*Lumex*, Russia) using a KBr beam splitter in the spectral range of 500–2000 cm^{-1}.

Chromatograph parameters

Chromatographic analysis was performed on a Stayer-M instrument (*Akvilon*, Russia) using an analytical column *Shodex IC SI-90 4E* 4.0 × 250 mm, PEEK particle size 9 μm (*Shodex*, USA) with a conductometric detection system. The volume of the injected sample was 20 μL, while the temperature of the column thermostat was 35°C and the conductivity scale of the detector was 40 mA.

Data processing

A Stayer-M liquid chromatograph was controlled and chromatographic data were processed on a PC using the MultiChrom program (*Ampersend*, Russia). The chromatograms of the analyzed compounds were designed using the OriginPro 2016 program (*OriginLab*, USA). The IR spectra of the compounds were designed using the Omnic 9.2 program (*Thermo Fisher Scientific*, USA). The calculation and processing of validation calculation data was carried out in Microsoft Excel 2016 program (*Microsoft*, USA).

RESULTS AND DISCUSSION

The chromatographic separation of chlorine-containing ions in isocratic mode using various types of eluents has been already described in the literature. At the initial stage, when selecting the conditions for the separation of chloride, chlorite, chlorate, and perchlorate ions, eluents based on Na_2CO_3–$NaHCO_3$ were used with concentrations in the ratios of 1.7–1.8 mM, 0.8–0.9 mM, and 2.5–0.4 mM, respectively[1]. In the first case, only the presence of Cl^-, ClO_2^-, and ClO_3^- ions was detected by varying the flow rate from 0.3 to 1.0 mL/min. When the concentration of eluents used was halved and their proportional ratios changed, chromatographic signals of chloride, chlorite, and chlorate ions were also observed. No chromatographic signals of perchlorate ions were detected upon increasing the concentrations of sodium carbonate and bicarbonate to 2.5 and 0.4 mM, respectively.

Further attempts at chromatographic determination of the studied ions using an eluent based on potassium biphthalate ($C_8H_5O_4K$) were carried out. When carrying out the analysis at an eluent rate ranging from 0.3 to 1.0 mL/min using 0.5 mM potassium biphthalate, it was not possible to detect chloride ions. However, an increase in the substance concentration in the eluent to 7.0 mM resulted in the identification of only chloride and chlorite ions in the studied solutions.

When determining chromatographically chloride-containing ions in isocratic mode, the use of a sodium hydroxide eluent is often described. When analyzing the same solutions of chlorine-containing ions using 20.0 mM NaOH as an eluent at a flow rate of 0.7 mL/min, it was possible to detect signals of chloride, chlorate, and perchlorate ions. In this case, varying the eluent flow rate did not lead to the detection of the chlorite ion: apparently, its chromatographic peak was overlapped by the signal of the chloride ion. A twofold decrease in the concentration of the alkaline eluent to 10.0 mM of sodium hydroxide at a flow rate of 0.3 mL/min led to the detection of only chloride and chlorate ions in the solution. However, in the case of such a substance being present in the eluent, an increase in the flow rate also resulted in the detected presence of perchlorate ions. An alkaline eluent based on 7.5 mM NaOH at a flow rate of 1.0 mL/min facilitates the detection of chloride, chlorate, and perchlorate ions. However, when the flow rate of this eluent was reduced to 0.7 mL/min, it was possible to detect all chloride, chlorite, chlorate, and perchlorate ions studied at this stage in the studied solutions (Fig. 1). At the same time, it should be noted that a greater decrease in the flow rate increases the time of a single chromatographic experiment.

Thus, to determine the quantitative assessment of Cl^-, ClO_2^-, ClO_3^-, and ClO_4^- ions, it is optimal to use 7.5 mM NaOH as an eluent at a flow rate of 0.7 mL/min.

As discussed earlier, the use of commercial samples of sodium hypochlorite to evaluate the content of hypochlorite ions is difficult due to the high chloride ion content. To solve this problem, we synthesized a sample of sodium hypochlorite with a higher content of the main substance according to the previously proposed method [29]. The method is based on the absorption of gaseous chlorine released as a result of the interaction of crystalline potassium permanganate with concentrated hydrochloric acid when heated with a solution of sodium hydroxide. Following complete gas evolution, the resulting solution was

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[1] The analysis was carried out using an electrodialysis suppressor of carbonate and bicarbonate ions.

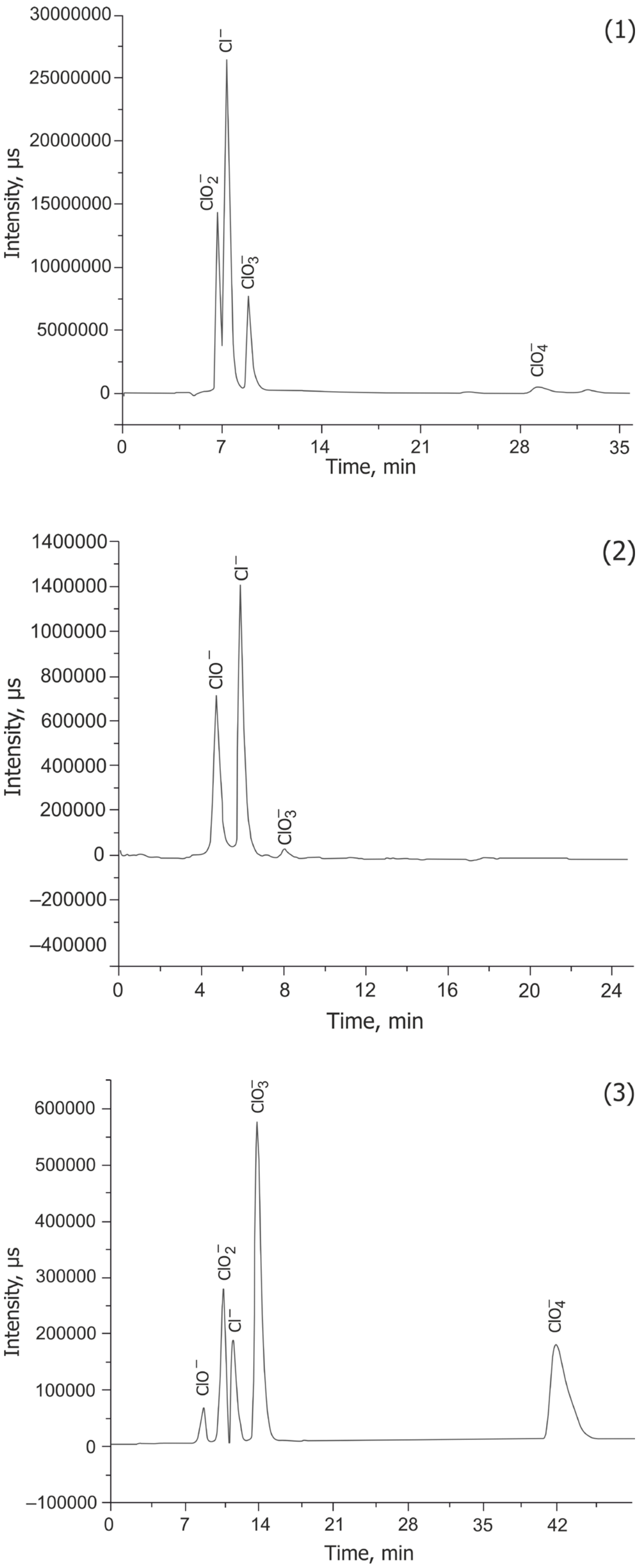

Fig. 1. Chromatograms of chlorine-containing compounds obtained by ion-exchange chromatography with conductometric detection under various conditions: (1) eluent 7.5 mM NaOH, flow rate 1.0 mL/min; (2) eluent 7.5 mM NaOH, flow rate 0.7 mL/min (synthesized NaClO sample); (3) eluent 7.5 mM NaOH, flow rate 0.4 mL/min.

filtered to remove possible precipitated impurities, then cooled and centrifuged. The precipitate formed after centrifugation was separated from the main solution by decantation and dried under vacuum in a dark place. The analysis of the obtained substance was carried out using ion-exchange chromatography under previously developed conditions for the chromatographic determination of chlorine-containing ions (Fig. 1). In addition to the new signal assigned to the hypochlorite ion, the resulting substance as revealed by the chromatogram contains the chloride ion as a byproduct, as well as impurity amounts of the chlorate ion. According to ion-exchange chromatography, the content of sodium chloride was 1.21% ± 0.07%, while that of sodium chlorate was 0.015% ± 0.001%. According to the IR spectroscopy data, no other chlorine-containing ions were present in the samples of the obtained sodium hypochlorite crystalline hydrate (Fig. 2). Therefore, the content of hypochlorite ions was determined by iodometric titration. The average content of sodium hypochlorite in the crystalline hydrate was 39.8% ± 0.3%.

Analysis of the chromatographic determination of the resulting hypochlorite ions in combination with chloride, chlorite, chlorate, and perchlorate ions was carried out under previously selected conditions using 7.5 mM NaOH as an eluent. By varying the flow rate, it was possible to achieve the optimal separation of all ions already at an eluent flow rate of 0.4 mL/min (Fig. 1). In this case, the analysis time was 50 min. A decrease in the eluent flow rate led to an increase in the analysis time without affecting the resolution of chloride-containing ion determination.

To assess the applicability of the developed method, the validation parameters were also calculated in accordance with the recommendations for analytical methods [30]. The measurement accuracy was evaluated using the addition method for each compound. The obtained values of the extraction degree of all ions in the range of 99–101% testify to the lack of systematic measurement errors. Calibration curves for the studied chlorine-containing ions (hypochlorite ion 0.50–3.00 mg/L; chloride ion 0.249–2.50 mg/L; chlorite ion 0.373–2.61 mg/L; chlorate ion 0.498–2.52 mg/L; perchlorate ion 0.498–2.49 mg/L) are linear in all cases with a correlation coefficient above 0.9990 (Fig. 3 and Table). The calculation of the limit of detection (LOD) and limit of quantification (LOQ) values was based on the signal-to-noise ratio. Due to the high intensity of the chromatographic chloride ion signal, the detection and quantitation limits are 0.87 µg/L and 2.63 µg/L, respectively; this figure is much lower as compared to other ions. For example, according to the LOD and LOQ values for the

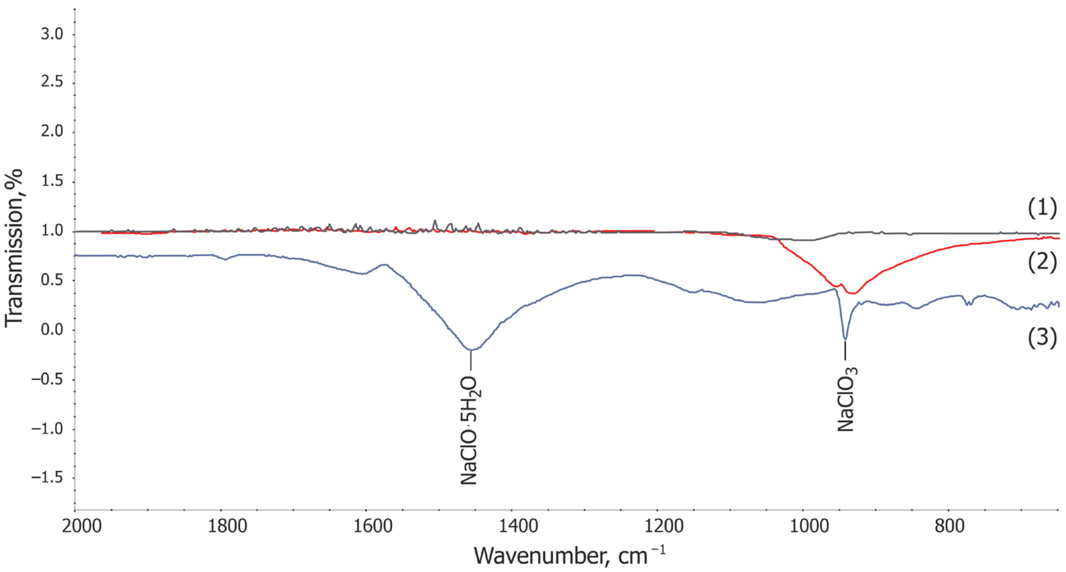

Fig. 2. IR spectra of sodium chloride (1), potassium chlorate (2), and sodium hypochlorite (3).

hypochlorite ions are at the level of 47.8 µg/L and 145 µg/L, respectively, the developed method can be additionally characterized as selective and sensitive. More detailed results of calculations of validation parameters for the studied chlorine-containing ions are given in the table.

The suitability of the developed method was assessed using three commercially available samples of disinfectants comprising anolytes produced by different manufacturers. In order to ensure a "blind" independent experiment, the studied samples of anolytes were encrypted under the codes Anolyte-1, Anolyte-2, and Anolyte-3. According to the results of the tests, samples Anolyte-1 and Anolyte-3 were found to contain only chloride ions 0.571 ± 0.027 and 0.730 ± 0.035 wt %, respectively. The Anolyte-2 sample, on the other hand, contained hypochlorite, chloride, and chlorite ions at concentrations of 0.0382 ± 0.0019, 0.0738 ± 0.0035, and 0.0181 ± 0.0008 wt %, respectively (Fig. 4). When comparing the obtained results with the data indicated by the manufacturers, the total concentrations of chlorine-containing ions in all the studied samples were found to exceed the values indicated in the instructions for use by the manufacturer. This finding additionally indicates the need for careful quality control and procedural accuracy when using anolytes.

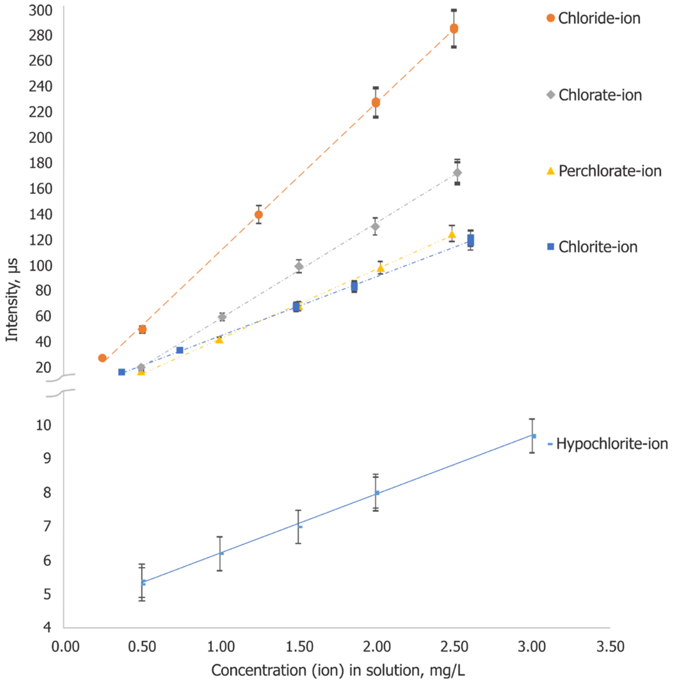

Fig. 3. Graphical representation of the calibration curves of hypochlorite, chloride, chlorite, chlorate, and perchlorate ions.

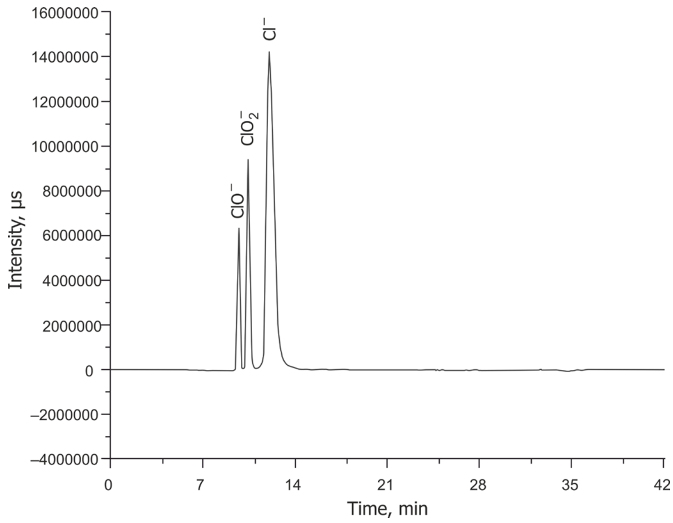

Fig. 4. Chromatogram of the Anolit-2 disinfectant.

Table. Results of calculation validation parameters ($n = 5$; $P = 0.95$)

Parameter		Ions				
		ClO^-	Cl^-	ClO_2^-	ClO_3^-	ClO_4^-
Retention time repeatability	RSD, %	0.66	0.28	0.23	0.15	0.029
Area repeatability	RSD, %	0.58	0.55	0.77	1.28	0.86
Theoretical plates		3123	3850	3695	2290	3296
Resolution		1.52	1.58	1.78	2.19	2.26
Peak asymmetry		1.50	1.04	1.23	1.21	1.47
Linearity	Correlation coefficient	0.9991	0.9994	0.9992	0.9992	0.9990
	Sensitivity factor	1.7450	116.15	46.282	74.780	54.421
	Axial displacement	4.4765	−4.7886	−1.1377	−16.154	−11.805
Accuracy	Recovery, %	99.4	100.3	99.8	100.1	99.1
	RSD, %	2.48	1.24	0.62	0.97	0.87
Limit of detection (LOD), $\mu g \cdot L^{-1}$		47.8	0.867	7.11	18.0	52.9
Limit of quantitation (LOQ), $\mu g \cdot L^{-1}$		145	2.63	21.5	54.9	160

Note: RSD – relative standard deviation, *S/N* – signal-to-noise ratio.

CONCLUSIONS

As part of the development of a procedure for the determination of hypochlorite, chloride, chlorite, chlorate, and perchlorate ions simultaneously present in solution, optimal conditions for their chromatographic separation were obtained using ion-exchange chromatography with conductometric detection. The best separation of the mixture components was obtained using a 7.5 mM NaOH solution as an eluent at a flow rate of 0.4 mL/min with a Shodex IC SI-90 4E anionic column. According to the validation parameter calculations, the developed method can be used to quantify all the listed chlorine-containing ions in the studied concentration ranges. The performed calculations also confirm the high sensitivity and extraction degree of each chlorine-containing compound under study.

The results of the study suggest the suitability of the developed method not only for the analysis of disinfectants, but also in the preparation centralized and non-centralized water supplies, as well as for determining residual quantities of chlorine-containing ions in wastewater.

Authors' contributions

E.A. Lapina – conducting the experiments, performance of chromatography research, analysis of the experimental data, and preparing illustrations;

S.A. Zverev – analysis of literary sources, developing the scientific concept, and writing the text of the article;

S.V. Andreev – offering consultations on research, editing the text of the article;

K.A. Sakharov – IR spectrum analysis, editing the text of the article.

The authors declare no conflicts of interest.

REFERENCES

1. McCarthy W.P., O'Callaghan T.F., Danahar M., Gleeson D., O'Connor C., Fenelon M.A., *et al*. Chlorate and Other Oxychlorine Contaminants Within the Dairy Supply Chain. *Compr. Rev. Food Sci. Food Saf.* 2018;17(6):1561–1575. https://doi.org/10.1111/1541-4337.12393

2. Dannehl D., Schuch I., Gao Y., Cordiner S., Schmidt U. Effects of hypochlorite as a disinfectant for hydroponic systems on accumulations of chlorate and phytochemical compounds in tomatoes. *Eur. Food Res. Technol*. 2016;242(3):345–353. https://doi.org/10.1007/s00217-015-2544-5

3. Stanford B.D., Pisarenko A.N., Snyder S.A., Gordon G. Perchlorate, bromate, and chlorate in hypochlorite solutions: Guidelines for utilities. *J. Am. Water Works Assoc*. 2011;103(6):71–83. https://doi.org/10.1002/j.1551-8833.2011.tb11474.x

4. Wang Z.X., Jin X., Gao Y.F., Kong F.Y., Wang W.J., Wang W. Fluorometric and colorimetric determination of hypochlorite using carbon nanodots doped with boron and nitrogen. *Microchim. Acta*. 2019;186(6):Article number 328. https://doi.org/10.1007/s00604-019-3443-4

5. Lu L., Zhang J., Yang X. Simple and selective colorimetric detection of hypochlorite based on anti-aggregation of gold nanoparticles. *Sensors Actuators B: Chem*. 2013;184:189–195. https://doi.org/10.1016/j.snb.2013.04.073

6. Girenko D.V., Gyrenko A.A., Nikolenko N.V. Potentiometric Determination of Chlorate Impurities in Hypochlorite Solutions. *Int. J. Anal. Chem*. 2019;2019. https://doi.org/10.1155/2019/2360420

7. Xie L., Zheng R., Hu H., Li L. Determination of hypochlorite and bisulfite in water by bifunctional colorimetric sensor based on octupolar conjugated merocyanine dyes. *Microchem. J*. 2022;172(PA):106931. https://doi.org/10.1016/j.microc.2021.106931

8. Hammar L., Wranglén G. Cathodic and anodic efficiency losses in chlorate electrolysis. *Electrochim. Acta*. 1964;9(1):1–16. https://doi.org/10.1016/0013-4686(64)80001-3

9. Levanov A.V., Isaikina O.Y. Mechanism and Kinetic Model of Chlorate and Perchlorate Formation during Ozonation of Aqueous Chloride Solutions. *Ind. Eng. Chem. Res.* 2020;59(32):14278–14287. https://doi.org/10.1021/acs.iecr.0c02770

10. Alfredo K., Stanford B., Roberson J.A., Eaton A. Chlorate challenges for water systems. *J. Am. Water Works Assoc*. 2015;107(4):E187–196. https://doi.org/10.5942/jawwa.2015.107.0036

11. Li X.A., Zhou D.M., Xu J.J., Chen H.Y. Determination of chloride, chlorate and perchlorate by PDMS microchip electrophoresis with indirect amperometric detection. *Talanta*. 2008;75(1):157–162. https://doi.org/10.1016/j.talanta.2007.10.054

12. Biesaga M., Kwiatkowska M., Trojanowicz M. Separation of chlorine-containing anions by ion chromatography and capillary electrophoresis. *J. Chromatogr. A*. 1997;777(2):375–381. https://doi.org/10.1016/S0021-9673(97)00338-5

13. Sanz Rodriguez E., Lam S., Smith G.G., Haddad P.R., Paull B. Ultra-trace determination of oxyhalides in ozonated aquacultural marine waters by direct injection ion chromatography coupled with triple-quadrupole mass spectrometry. *Heliyon*. 2021;7(4):e06885. https://doi.org/10.1016/j.heliyon.2021.e06885

14. Ma L., Wen S., Yuan J., Zhang D., Lu Y., Zhang Y., *et al*. Detection of chlorite, chlorate and perchlorate in ozonated saline. *Exp. Ther. Med*. 2020;20(3):2569–2576. https://doi.org/10.3892/etm.2020.9005

15. Rao B., Estrada N., McGee S., Mangold J., Gu B., Jackson W.A. Perchlorate production by photodecomposition of aqueous chlorine solutions. *Environ. Sci. Technol.* 2012;46(21):11635–11643. https://doi.org/10.1021/es3015277

16. Dietrich A.M., Ledder T.D., Gallagher D.L., Grabeel M.N., Hoehn R.C. Determination of Chlorite and Chlorate in Chlorinated and Chloraminated Drinking Water by Flow Injection Analysis and Ion Chromatography. *Anal. Chem*. 1992;64(5):496–502. https://doi.org/10.1021/ac00029a009

17. Yuan Y., Wang D., Long W., Deng F., Yu S., Tian J., *et al*. Ratiometric fluorescent detection of hypochlorite in aqueous solution and living cells using an ionic probe with aggregation-induced emission feature. *Sensors Actuators B: Chem*. 2021;330:129324. https://doi.org/10.1016/j.snb.2020.129324

18. Zaporozhets O.A., Pogrebnyak O.S., Vizir N.N. Spectrophotometric determination of hypochlorite by N,N-diethylaniline. *J. Water Chem. Technol.* 2011;33(1):31–36. https://doi.org/10.3103/s1063455x11010061

19. Asakai T. Perchlorate ion standard solution: multipath titrimetric approach using three different stoichiometric reactions—Towards the establishment of SI traceable chemical standards. *Metrologia*. 2020;57(3):035005. https://doi.org/10.1088/1681-7575/ab79bf

20. Watanabe T., Idehara T., Yoshimura Y., Nakazawa H. Simultaneous determination of chlorine dioxide and hypochlorite in water by high-performance liquid chromatography. *J. Chromatogr. A*. 1998;796(2):397–400. https://doi.org/10.1016/S0021-9673(97)01009-1

21. Mavroudakis L., Mavrakis E., Kouvarakis A., Pergantis S.A. Determination of chlorate, perchlorate and bromate anions in water samples by microbore reversed-phase liquid chromatography coupled to sonic-spray ionization mass spectrometry. *Rapid Commun. Mass Spectrom.* 2017;31(11):911–918. https://doi.org/10.1002/rcm.7866

22. Themelis D.G., Delmer W.W., Gordon G. Determination of low concentrations of chlorite and chlorate ions by using a flow-injection system. *Analytica Chimica Acta*. 1989;225:437–441. https://doi.org/10.1016/s0003-2670(00)84634-6

23. Stahl R. Ion chromatographic determination of chloride, chlorate, and perchlorate in sulfuric acid solutions. *Chromatographia*. 1993;37(5–6):300–302. https://doi.org/10.1007/bf02278638

24. Gilchrist E.S., Healy D.A., Morris V.N., Glennon J.D. A review of oxyhalide disinfection by-products determination in water by ion chromatography and ion chromatography-mass spectrometry. *Anal. Chim. Acta*. 2016;942:12–22. https://doi.org/10.1016/j.aca.2016.09.006

25. Bebeshko G.I., Karpov Y.A. Current methods of determination of chlorine in inorganic substances (Overview). *Inorg. Mater*. 2012;48(15):1341–1348. https://doi.org/10.1134/s002016851214004x

26. Young T.R., Cheng S., Li W., Dodd M.C. Rapid, high-sensitivity analysis of oxyhalides by non-suppressed ion chromatography-electrospray ionization-mass spectrometry: Application to ClO_4^-, ClO_3^-, ClO_2^-, and BrO_3^- quantification during sunlight/chlorine advanced oxidation. *Environ. Sci.: Water Res. Technol*. 2020;6:2580–2596. https://doi.org/10.1039/D0EW00429D

27. Gallidabino M.D., Irlam R.C., Salt M.C., O'Donnell M., Beardah M.S., Barron L.P. Targeted and non-targeted forensic profiling of black powder substitutes and gunshot residue using gradient ion chromatography – high resolution mass spectrometry (IC-HRMS). *Anal. Chim. Acta*. 2019;1072:1–14. https://doi.org/10.1016/j.aca.2019.04.048

28. Pisarenko A.N., Stanford B.D., Quiñones O., Pacey G.E., Gordon G., Snyder S.A. Rapid analysis of perchlorate, chlorate and bromate ions in concentrated sodium hypochlorite solutions. *Anal. Chim. Acta.* 2010;659(1–2):216–223. https://doi.org/10.1016/j.aca.2009.11.061

29. Okada T., Asawa T., Sugiyama Y., Iwai T., Kirihara M., Kimura Y. Sodium hypochlorite pentahydrate ($NaOCl·5H_2O$) crystals; An effective re-oxidant for TEMPO oxidation. *Tetrahedron*. 2016;72(22):2818–2827. https://doi.org/10.1016/j.tet.2016.03.064

30. Reviewer Guidance. *Validation of Chromatographic Methods*. Washington: Center for Drug Evaluation and Research (CDER); 1994. Vol. 2. 33 p.

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The article was submitted: July 15, 2022; approved after reviewing: October 28, 2022; accepted for publication: May 12, 2023.

Translated from Russian into English by M. Povorin
Edited for English language and spelling by Thomas A. Beavitt