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*B. Murashevych^a, D. Girenko^b, O. Lebed^b, H. Maslak^a, O. Netronina^a***INFLUENCE OF VARIOUS FACTORS ON THE EMISSION OF HYPOCHLOROUS ACID FROM SODIUM HYPOCHLORITE SOLUTIONS INTO THE AIR**^a Dnipro State Medical University, Dnipro, Ukraine^b Ukrainian State University of Science and Technologies, Dnipro, Ukraine

Active chlorine compounds are powerful microbicidal agents traditionally used for surface disinfection. Following the COVID-19 pandemic, the potential use of these compounds for air treatment to mitigate the spread of infectious diseases has been actively studied. A promising approach involves developing disinfection systems capable of maintaining a sufficient concentration of the most effective gaseous antimicrobial component of active chlorine – hypochlorous acid (HOCl) – in indoor air. This study investigates the influence of various factors on the emission of HOCl into the air during its bubbling through sodium hypochlorite (NaOCl) solutions. A colorimetric method for determining the total chlorine content in the air has been refined. The effects of key parameters of NaOCl working solutions on the HOCl concentration in the air have been examined. It has been demonstrated that, at a constant pH of the working solution, the total chlorine content in the air is strictly proportional to the HOCl concentration in the solution, which, in turn, can be determined using established molar distribution diagrams of active chlorine species. When electrochemically generated NaOCl working solutions (containing approximately 1100 mg/L of active chlorine) are used without additional composition adjustments, the HOCl concentration in the air can be maintained within the range of 6.0–11.6 mg/m³. The findings of this study can be applied in the development of fumigation-based air disinfection systems and in the assessment of air contamination risks associated with chlorine-containing compounds.

Keywords: active chlorine, hypochlorous acid, sodium hypochlorite, gas emission, disinfection.

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Introduction

More frequent outbreaks of infectious diseases, especially those transmitted by aerogenic mechanism, pose an increasing threat to the modern world [1]. The COVID-19 pandemic has clearly demonstrated that the most effective way to combat such phenomena is through preventive measures, which include the wearing of personal protective equipment and mass sanitary and hygiene measures [2]. The latter mainly consist in the use of effective disinfection and antiseptic systems.

It is obvious that pathogen-contaminated air

makes a huge contribution to the spread of infections. Pathogenic microorganisms can sediment from it onto various surfaces, retaining virulence and causing further transmission through the contact mechanism, and most importantly, they can get directly from the disease carrier to a healthy person through the respiratory tract and mucous membranes [3]. Interruption of this transmission mechanism is the most difficult in terms of technology. Currently existing air purification technologies (ventilation, filtration, irradiation of various types, local «air washing» units, etc.) solve this problem only partially. Most importantly, none

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of them can quickly kill the pathogens released by an infected person and prevent the transmission of the disease from person to person upon close contact. Except for the constant use of personal protective equipment, this seems possible only when the entire volume of the premise is filled with some kind of microbiocidal agent that would interact with the pathogen immediately when it enters the air and would quickly neutralize it.

In this context, much attention is paid to active chlorine compounds as promising agents for air disinfection. The main position here is occupied by sodium hypochlorite NaOCl and hypochlorous acid HOCl. These reagents have a wide spectrum of microbiocidal activity, mainly due to their oxidizing and chlorinating properties [4]. It was repeatedly reported that filling the air with HOCl aerosols is effective against viruses of different types [5] and certain bacteria [6] both suspended in the air and deposited on surfaces. At the same time, despite the high reactivity of these compounds, their toxicity, including inhalational [7,8], in effective antimicrobial concentrations turns out to be acceptably low, which suggests the safety of air treatment by them directly in the presence of people. However, most part of such studies relate to the aerosol treatment of premises by ultrasonic or mechanical dispersion of active chlorine solutions indoors. This method has several obvious disadvantages. Firstly, the administration of a large amount of dilute solution into the air leads to a sharp increase in humidity, reducing human comfort. Secondly, the presence of residual amounts of hypochlorite precursors, for example, sodium chloride or hydroxide, in such an aerosol is corrosive and poses a serious danger to electrical devices. And thirdly, the possibility of presence of impurities of sodium chlorate and free alkali in the chlorine-active solution significantly increases the toxic effect. Therefore, despite the high effectiveness of disinfection by this method, its permanent use in the presence of people is doubtful.

In connection with the above, the gas-phase (fumigation) treatment of air with active chlorine is of interest. Hypochlorous acid is volatile, and can be selectively blown outward by a carrier gas from NaOCl solutions, the remaining components of which (mainly sodium chloride and sodium hypochlorite) are nonvolatile. This can be achieved, for example, by using NaOCl solutions in forced-air vaporizing systems of different types [9]. However, in contrast to aerosol spraying, where a solution of a known concentration is dispersed in air in a known amount, the quantitative control of the process in this case is more difficult. Studies of the HOCl emission from NaOCl solutions

into the air are few and controversial [9,10]. This work is devoted to the study of the influence of various factors on the process of HOCl emission from NaOCl solutions into the air during bubbling for further use the obtained data in the design of systems for complex disinfection of premises with active chlorine vapors.

Materials and methods

Description of the sodium hypochlorite base stock solution used

The NaOCl solution synthesized via special electrochemical technology was used in the study [8]. The base stock solution had total chlorine concentration 1090–1190 mg/L at pH 9.50–9.60, and contained approximately 8.3 g/L NaCl. Hereinafter total chlorine is considered as the sum of free (represented by HOCl and/or OCl^-) and combined (i.e. mono- and dichloramines) chlorine. The total chlorine concentration in the base and working NaOCl solutions was checked immediately before each experiment by the standard method of iodometric titration [8].

Description of the general experimental procedure

The schematic diagram of the installation for determining the HOCl emission from NaOCl solutions into the carrier gas was organized as shown in Fig. 1. The specified volume of working NaOCl solution with a predetermined total chlorine concentration and pH was poured into a Drexel bottle (WS) with a ceramic bubbler immersed to the bottom and providing a high dispersion of the bubbles of gas passed through it. The bottle was placed in a thermostatically controlled ultrasonic bath UZM-002-1 (T). To the inlet pipe of the bottle the heat exchanger (HE) made of a thin-walled titanium tube was attached, which was also immersed in a bath to ensure the same temperature of the working solution and the carrier gas passed through it. A droplet eliminator flask (DE) was connected to the outlet pipe to destroy possible aerosol and prevent the transfer of NaOCl droplets further along the cascade, and then Drexel bottles (AB1 – ABn) with ceramic bubblers filled with a certain volume of the absorbing solution of taurine (Hangzhou Keying Chem Co., Ltd., P. R. China) were followed. The outlet hose of the last absorption bottle was connected to an ASA-2M electric aspirator (Asp), which allows precise control of the volumetric flow rate of the gas passed through the setup and the duration of the experiment.

In the main experiment, the carrier gas was passed through the system at a given volumetric flow rate. As a carrier, the outdoor air, carbon dioxide content of which was controlled by the AZ 7530 CO_2 detector (AZ Instrument Corp., Taiwan), or nitrogen (chemically pure, from the cylinder) was used. Thus,

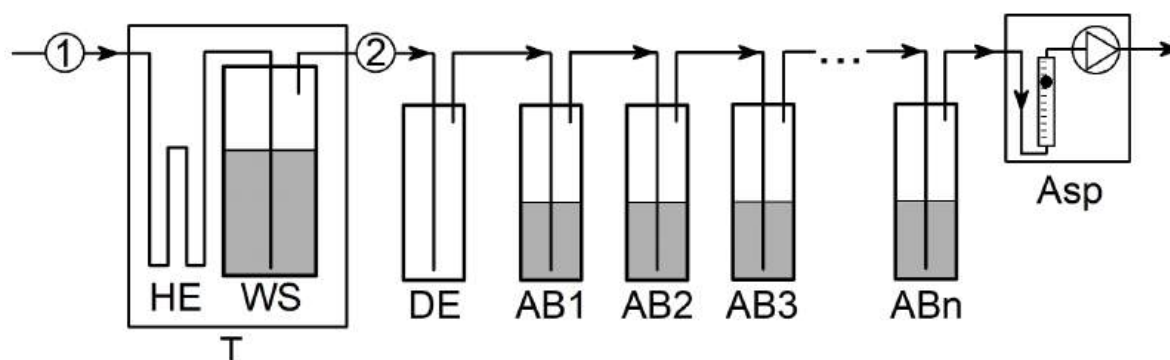


Fig. 1. Schematic diagram of the installation for studying the HOCl emission from sodium hypochlorite solutions into the carrier gas: 1 – incoming carrier gas; HE – heat exchanger; WS – Drexel bottle with NaOCl working solution;

T – thermostatic ultrasonic bath; 2 – carrier gas enriched with HOCl; DE – drop eliminator bottle;

AB1-ABn – absorption Drexel bottles; Asp – electric aspirator

the carrier gas bubbled through the NaOCl working solution was saturated with total chlorine and carried away its volatile component, HOCl, into the absorption bottles, in which N-chlorotaurine (NCT), a fairly stable N-chloramine convenient for further analysis, was instantly formed [11]. After bubbling a certain volume of gas, the absorption bottles were disconnected and the total chlorine concentration in the last one was determined. If it was absent, the contents of the remaining absorption bottles were combined, and the volume, the pH of the resulting solution and the total chlorine concentration in it were measured. If total chlorine was present in the last absorption bottle, then the experiment was repeated by adding Drexel bottles with taurine solution until chlorine was not detected in the last of them. This ensured the complete absorption of all HOCl released into the gas. If it was necessary to continue the experiment with the same NaOCl solution, the absorption bottles were rinsed with water, the same amount of taurine solution was poured into them, and all actions were repeated. Each experiment was performed in triplicate; the graphs and tables below show the obtained average values.

The total chlorine concentration in the combined absorption solution was determined colorimetrically using an eXact Micro 20 photometer and corresponding reagent strips eXact Strip Micro High Range Chlorine or eXact Strip Micro Total Chlorine DPD-4 reagent strips (Industrial Test Systems, Inc., USA) (standard DPD-test [12]). The mass of total chlorine (represented by HOCl) absorbed by the absorption solution was calculated by the following equation:

$$m_{AC} = \frac{(C_{AS} - C_{blank}) \cdot V_{AS}}{1000}, \quad (1)$$

where m_{AC} is the weight of total chlorine captured (mg); C_{AS} is the colorimetrically determined total chlorine concentration in the absorption solution (mg/L); C_{blank} is the results of photometry of a «blank sample» (initial absorption solution of taurine), that is, the imaginary total chlorine concentration in it (mg/L); and V_{AS} is the absorption solution volume (mL).

The average amount of total chlorine w_{AC} , released into gas from the NaOCl solution per unit time was determined graphically as the value of the slope of the kinetic curve plotted in the coordinates m_{AC} vs. τ . The average concentration of total chlorine in the bubbled carrier gas was calculated by the following equation:

$$C_{AC} = \frac{w_{AC}}{Q}, \quad (2)$$

where C_{AC} is the average total chlorine concentration emitted in the carrier gas (mg/m³); w_{AC} is the graphically determined value of the average weight of emitted total chlorine per unit time (mg/min); and Q is the carrier gas flow rate (m³/min).

The acidity of the solutions was measured using an ADWA AD1030 pH meter. The UV spectra of the solutions were recorded on the ULAB 108UV spectrophotometer.

Description of the experiment to verify the correctness of the method for determining the active chlorine amount released into the air

To verify the method used, namely to study the effect of the technological parameters of the installation on the concentration of total chlorine released into the air, the following experiments were previously carried out:

a) to verify the correctness of colorimetry data when using taurine as an absorbent of HOCl, NCT solutions with total chlorine concentration of 1–6 mg/L were prepared by adding the calculated amount of a titrated solution of the initial NaOCl to a 0.5 g/L, 1.0 g/L and 10.0 g/L solutions. All solutions were analyzed colorimetrically as described above, and the obtained concentrations were compared with the calculated ones;

b) to test the stability of NCT formed during the experiment, air or nitrogen was bubbled for 50 minutes at a rate of 10 L/min through NCT solution of known concentration. Every 10 minutes the total chlorine concentration in this solution was being determined and compared with the initial one;

c) to test the effect of the taurine concentration in the absorption solution on the results of colorimetry, 100 L of nitrogen were bubbled with the same flow rate through the base stock NaOCl solution into absorption bottles filled with the 0.5 g/L, 1.0 g/L, and 2.0 g/L taurine solution. The amount of total chlorine in absorption solutions was determined and compared;

d) to determine the effect of the shape and volume of a Drexel bottle with NaOCl working solution on the process of active chlorine emission, cylindrical and round bottom flasks with a volume of 250 mL were used; the diameter of the solution surface was 5.5 cm for a cylindrical flask and 8.5 cm for a round flask; the immersion depth of the bubbler was 4.5 cm and 2.3 cm, respectively. The volume of base stock NaOCl solution in both cases was 100 mL. Nitrogen was bubbled through the system for 10 min at a rate of 10 L/min, the amount of total chlorine in it was determined, and the results were compared;

e) to determine the effect of the working solution column height, 70, 100 and 120 mL of base stock NaOCl solution were poured into a 250 mL cylindrical Drexel bottle. The height of the solution column above the bubbler was 3.0 cm, 4.5 cm, and 5.5 cm, respectively. Nitrogen was bubbled through the system for 10 min at a rate of 10 L/min, the amount of total chlorine in it was determined, and the results were compared;

f) to determine the effect of the volumetric flow rate of the carrier gas bubbling through the system: 100 liters of nitrogen were bubbled through 100 mL of base stock NaOCl solution at a rate of 2 L/min, 5 L/min and 10 l/min. The amount of absorbed active chlorine was determined in each case, and the results were compared.

Results and discussion

The process of total chlorine emission from NaOCl solutions into the air, of course, mainly

depends on the concentration of volatile components, HOCl and Cl_2 , in it, as well as on their solubility under specific conditions. It is known that such solutions are pH-dependent equilibrium systems in which reversible interconversions can occur between the three main components of active chlorine: ClO^- , HOCl and Cl_2 . The ratios between these components depending on the pH of the solution are known [13], and the corresponding diagram of their equilibrium in the studied solutions is shown in Fig. 2.

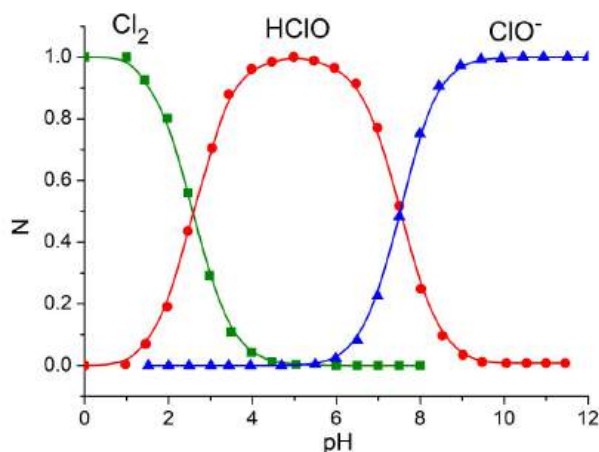


Fig. 2. Diagram of distribution of the molar fractions of chlorine, hypochlorous acid, and hypochlorite ions in the studied NaOCl solutions against the background of 8.0 g/L NaCl

As seen, the dependence is very pronounced, and HOCl prevails in the pH range of 2.5–7.5. However, the stability of the solution at such pH is much lower than in alkaline media. At the same time, naturally, during fumigation disinfection, it is unacceptable to bring the working solution to the pH of the formation of the toxic and irritant Cl_2 . In addition to varying the pH, the amount of HOCl in saturated vapor can be increased by increasing the overall concentration of the working solution. Another factor affecting the emission of total chlorine, as for any gases, is temperature: in the absence of chemical interaction with the solvent, the solubility of the gas decreases with increasing temperature. Finally, according to Sechenov's law, the solubility of gases in liquids decreases with an increase in the concentration of the dissolved electrolyte (the effect of «salting out» the gas). In this regard, taking into account the variety of produced NaOCl solutions, which differ greatly in salt content, it was advisable to check the effect of the concentration of the most characteristic electrolyte – sodium chloride – on the HOCl emission into the air.

Confirmation of the correctness of the total chlorine detection method

It is obvious that the correctness of the method used to determine the total chlorine concentration in the air essentially depends on the properties of the absorbing solution. The use of water for this was impossible due to the low stability of HOCl in neutral and slightly acidic media, and also because of its volatility; for the same reason, standard near-neutral buffer solutions are not suitable for this role. The frequently used method of absorbing total chlorine with potassium iodide solution in the presence of starch, followed by photometry, was also not suitable due to the low predicted HOCl concentrations and the volatility of the resulting iodine. The technique developed and applied by us with the use of a taurine solution as an absorbent has a number of advantages. Such solutions, as any amino acid, have a certain buffering capacity and, at the concentrations used, have a pH that falls within the operating range of the photometer. When interacting with HOCl in a solution with an excess of taurine, NCT is instantly formed, which is quite stable and non-volatile. However, this approach has not yet been described and needs to be thoroughly tested in practice.

Colorimetry of blank samples of taurine solutions in the indicated concentrations showed a result of 0.03–0.04 mg/L and 2–3 mg/L of total chlorine for eXact Strip Micro Total Chlorine DPD-4 reagent strips and eXact Strip Micro High Range Chlorine strips, respectively. Photometry of distilled water showed similar results. Thus, this is probably due to a change in the optical density of the solution when the analytical reagent is washed off the strip, and is not significant.

The results of the colorimetry of NCT solutions with known total chlorine concentration and different taurine content showed that the deviation of the calculated value from the experimental value does not exceed 3.2%, with a tendency to increase the discrepancy between the results with an increase in the taurine concentration. Almost instantaneous formation of NCT during the reaction of taurine with sodium hypochlorite was proved by UV spectra recorded immediately after mixing the solutions. The spectrum shows an intense peak at 251 nm, which is characteristic of N-chlorotaurine [11].

The stability of NCT solution with a concentration of taurine 1.0 g/L and total chlorine 0.85 mg/L at initial pH of 6.40 during bubbling air and nitrogen through it turned out to be high: the total chlorine concentration not only did not decrease for 50 minutes, but even showed a tendency to a slight increase, reaching 0.89 mg/L in the end of the

experiment, which is apparently due to water entrainment. The NCT solutions with a higher total chlorine concentration – up to 25 mg/L – were also stable under the described conditions. However, NCT is known to be prone to decomposition in acid media, so we also studied the properties of its solutions at various pH. It has been established that under the experimental conditions, the rate of decomposition becomes noticeable at pH below 4.00. Therefore, during the main experiment, we constantly monitored the pH level of the absorbing solution so as not to allow it to fall below 4.50 in any of the absorbing bottles, which necessitated regular replacement of the absorbing solution.

Obviously, to ensure complete and rapid HOCl absorption from the gas phase by the taurine solution, it was necessary to create an excess of the latter in the absorption bottles. When passing 100 L of nitrogen at a rate of 10 L/min through 100 mL of a hypochlorite solution (1190 mg/L of active chlorine at pH 9.50) in 150 mL of an absorption solution with different taurine concentrations (0.5 g/L, 1.0 g/L, and 2.0 g/L) the photometrically determined concentration of total chlorine in the combined absorption solutions was the same in all cases and amounted to about 0.49 ± 0.05 mg/L, which corresponds to about 0.073 mg in absolute terms.

When changing the shape of the Drexel bottle with the NaOCl working solution, no significant changes in the amount of active chlorine released into the gas were noted: the average amount of absorbed active chlorine under the conditions specified in the Materials and methods was the same for the cylindrical and round Drexel flasks and averaged 0.073 ± 0.006 mg.

When conducting the main experiment, it was necessary to take into account the inevitable decrease in the volume of the working NaOCl solution due to the entrainment of water. This affects, on the one hand, the height of the column of the chlorine-active solution and, accordingly, the completeness of saturation of the carrier gas bubble with HOCl, which rises from the bubbler to the surface. On the other hand, it increases the concentration of the working solution, which should also affect the emission process. We found that at a carrier gas flow rate of 100 L/min, the decrease in the volume of the working solution is, on average, 0.1 mL/min. When nitrogen was bubbling through the Drexel bottle with different volumes of NaOCl solution, no noticeable difference was noted in the amount of HOCl released, which, as in the previous experiment, was about 0.075 mg, which indicates that under all the conditions studied, the gas bubble (and, accordingly, vapor over the solution) is

equally saturated with HOCl in all cases. As for the increase in the total chlorine concentration in the working NaOCl solution due to the entrainment of water, this process is compensated, firstly, by the entrainment of HOCl, and secondly, by the partial decomposition of total chlorine during gas bubbling. Due to this, for example, the concentration of the NaOCl stock solution (1150 mg/L of active chlorine, pH 9.55) after 30 min of air bubbling at a rate of 10 L/min practically did not change and amounted to 1144 mg/L (a decrease by 0.52%), which, as will be shown below, does not have a critical effect on the emission of active chlorine.

The flow rate of the carrier gas affects the solution zone gas filling, the size of the gas bubble and the speed of its passage through the working solution. When the same volume of nitrogen (100 L) was bubbled through the stock solution of NaOCl (1140 mg/L of active chlorine, pH 9.52) with different flow rates, the amount of active chlorine captured by the absorber did not change and amounted to about 0.073 mg.

Thus, the complex of the described data allows asserting that the method developed by us for measuring the amount of total chlorine released from NaOCl solutions, based on the absorption of HOCl from the air with a taurine solution, is accurate, reproducible, and can be used in various options for organizing the main experiment. Based on them, the optimal parameters were selected: a working NaOCl solution in an amount of 100 mL was poured into a cylindrical 200 mL Drexel bottle; to absorb HOCl, a 1.0 g/L taurine solution was used, poured into 3-5 successively connected 100 mL Drexel bottles, the total volume of the absorbing solution was 150–250 mL. Carrier gas was bubbled through the system at a flow rate of 10 L/min.

Influence of the pH of NaOCl solution on the HOCl emission process

It follows from the diagram (Fig. 2) that the key factor affecting the content of the target HOCl in NaOCl solution is its acidity. Accordingly, by adjusting this parameter, it is possible to vary the amount of HOCl released into the air over a wide range. We studied the processes of HOCl emission from NaOCl solutions with pH 5.50, 7.50, 9.50, and 11.50, by adjusting the initial pH of the base solution by adding a minimal amount of HCl or NaOH. Obviously, during the gas bubbling through NaOCl solutions, the pH level of the latter can change: the emission of HOCl should contribute to its increase, while the CO₂ absorption will decrease it. However, it should be taken into account that HOCl (a weak acid with pK_a 7.45–7.60) and NaOCl form a classical buffer

system. Accordingly, hypochlorite solutions with a pH in the range of about 6.5–8.5, in which both components are present in the equilibrium mixture in significant concentrations, should have some buffering capacity. In addition, when air is bubbling, the bicarbonate buffer, the presence of which is due to the CO₂ absorption, will also contribute to the stability of the pH of the NaOCl solution. To separate the influence of CO₂ on HOCl emission, as carrier gases we used air with measured CO₂ content and pure nitrogen in parallel.

The change in the pH level of 100 mL of the working sodium hypochlorite solution (1162 mg/L active chlorine) with different initial acidity during bubbling of air (carbon dioxide content 550–600 ppm) and nitrogen at a rate of 10 L/min at 15°C is shown in Fig. 3.

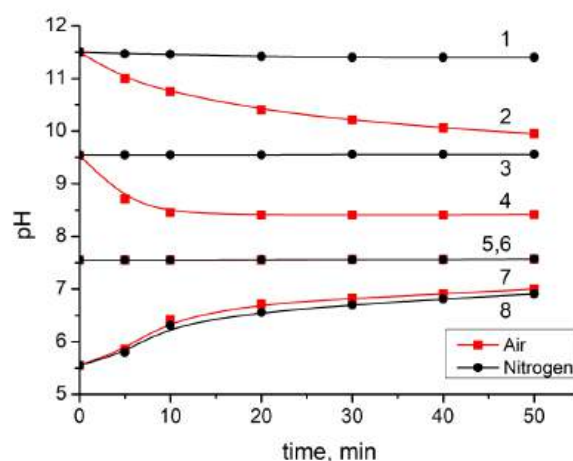


Fig. 3. Dynamics of changes in the pH of the NaOCl working solution with different initial acidity during air and nitrogen bubbling. Initial pH of the working solutions are 11.50 (curves 1 and 2), 9.50 (curves 3 and 4), 7.50 (curves 5 and 6), and 5.50 (curves 7 and 8)

As seen from Fig. 3, only the acidity of the solution with an initial pH of 5.50 noticeably changes when nitrogen is bubbling. It increases by one point and reaches a value of approximately 6.50 already in the first 20 minutes, and then the growth slows down. This is due to the gradual HOCl emission, the content of which at this pH value is 100% (Fig. 2). The similar dependence is observed when air is bubbling through this solution. When both nitrogen and air are bubbled through a solution with an initial pH of 7.50, its acidity remains almost constant. In the case of NaOCl solution with an initial pH of 11.50, when nitrogen is bubbling, the acidity expectedly remains constant, since there are no volatile components in it; when air is bubbling, the pH decreases significantly

over time due to the dissolution of carbon dioxide, and reaches a value of 9.95 in 50 minutes. The most significant data were obtained during bubbling gases through the base stock NaOCl solution with pH 9.50, because it is directly produced in the electrolyzers developed earlier, which could theoretically be integrated into the disinfection system. When nitrogen is bubbling through it, the acidity remains almost constant. However, when air is bubbling, it quickly (during the first 10 min) falls to pH 8.40–8.42 and then remains constant. This is explained, on the one hand, by the formation of a buffer system in which the HOCl:NaOCl ratio is approximately 10:90 (Fig. 2), and on the other hand, the complete neutralization of the free alkali present in the solution and the impossibility of further CO₂ dissolution at this pH [14]. The buffer capacity of this system with respect to air was found to be high, despite the constant decrease in the HOCl concentration. During continuous bubbling of air, the pH remained at the level about 8.40 after 130 minutes, and after 320 minutes it reached only 8.60, while there was a significant – 22 mL – decrease in the solution volume. Thus, at least in the pH range from 7.50 to 8.40, hypochlorite solutions retain stable acidity for a long time when air is passed through them.

The kinetic curves of the accumulation of total chlorine absorbed by taurine solution in the same experiment are shown in Fig. 4.

As seen from Fig. 4, provided that the pH of the NaOCl solution is stable, HOCl is emitted from it gradually and evenly, which is most fully confirmed by the linearization of the kinetic data obtained by bubbling nitrogen through working solutions with pH

7.50, 9.50, and 11.50. In the case of a solution with pH 5.50, a significant deviation from the straight line is observed, associated with the previously described rapid increase in pH during the experiment; at the same time, the segment corresponding to the initial period (the first 5 minutes), when the change in pH is still insignificant, is also linear. Most importantly, there is a clear correlation between the amount of total chlorine released into the air and its content in solution. Thus, the HOCl concentration in a solution with pH 5.50 calculated according to Fig. 2 is twice as high as in a solution with pH 7.50, and the same ratio was found for the slope coefficients w_{AC} of the corresponding kinetic curves: $(0.5651/0.2796)=2.02$ (for air). From the practical point of view, the data obtained by passing air through the base stock NaOCl solution with an initial pH of 9.50 are of interest. After saturation with CO₂ and reaching stable pH of 8.42, a constant HOCl emission of 0.0595 mg/min is achieved. Here, too, almost complete correspondence is observed to the content of the volatile component in such solution: the HOCl concentration in it is about 11%, which is 4.55 times less than at pH 7.50, when solution contains 50% of HOCl (Fig. 2); the ratio of the slopes of the corresponding kinetic curves is $(0.2796/0.0595)=4.70$. It was also found that HOCl, although in minimal amounts, was emitted even from solutions with pH 11.50. This is probably due to surface phenomena in the foam formed during bubbling. When air is passed through, a rapid drop in the pH of the solution constituting the shell of the gas bubble is possible because of the diffusion of CO₂ into it, due to which the formation of a certain amount of HOCl realizes.

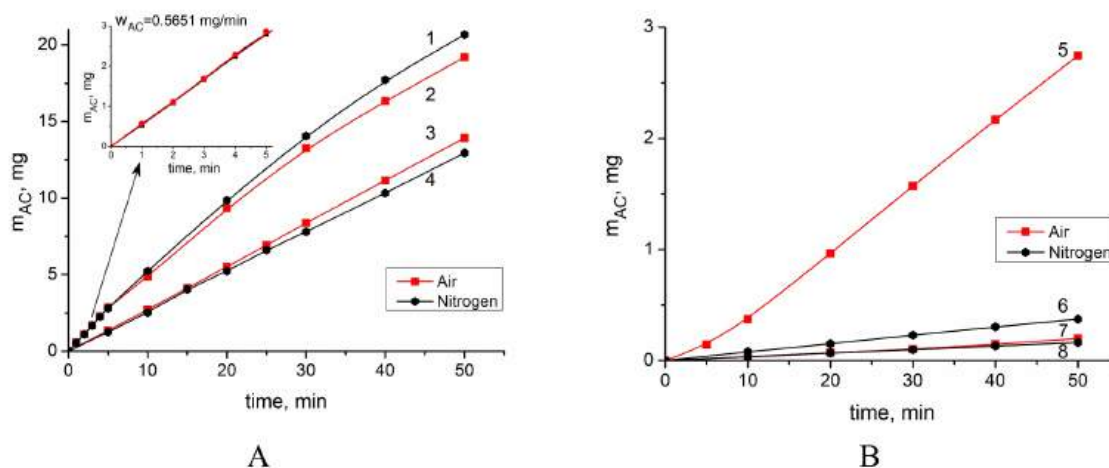


Fig. 4. Kinetic curves of accumulation of total chlorine in the absorption solution during nitrogen and air bubbling through acidified (A) and alkaline (B) sodium hypochlorite solutions: pH 5.50 – curves 1 and 2 ($w_{AC}=0.5651$ mg/min for initial period); pH 7.50 – curves 3 ($w_{AC}=0.2796$ mg/min) and 4 ($w_{AC}=0.2592$ mg/min); pH 9.50 – curves 5 ($w_{AC}=0.0595$ mg/min) and 6 ($w_{AC}=0.0075$ mg/min); pH 11.50 – curves 7 ($w_{AC}=0.0035$ mg/min) and 8 ($w_{AC}=0.0033$ mg/min)

This can also explain a certain excess of the amount of active chlorine absorbed from the air compared to nitrogen even at the same pH of the working NaOCl solution.

The average concentrations of total chlorine in the gas that passed through NaOCl solutions with different pH values are calculated based on the obtained graphic data; and they are shown in Table 1.

Table 1
Average concentrations of total chlorine in the carrier gas bubbled through NaOCl solutions with different pH

pH of the working NaOCl solution, units	Carrier gas	Average concentrations of total chlorine in the carrier gas (C_{AC}), mg/m ³
11.50	nitrogen	0.33
	air	0.35
9.50	nitrogen	0.75
	air	not measurable
8.42	nitrogen	not measured
	air	5.95
7.50	nitrogen	25.92
	air	27.96
5.50	nitrogen	56.51
	air	56.51

It should be noted that, according to literary data, the content of HOCl in the air is already at the level of 0.03 mg/m³ ensures a reduction in the air microbial count at a rate of 13%/min, and at a concentration of 0.3 mg/m³ and higher, the suppression rate is 65%/min and more, depending on the type of microorganism [15].

Influence of NaOCl concentration on the HOCl emission process

To study the effect of the active chlorine concentration in the NaOCl solution on HOCl emission into the air, the base stock solution was saturated with minimum quantity of CO₂ to stable pH 8.42. The concentration of the resulting solution was 1098 mg/L active chlorine. From this solution, 100 mL of working solutions of various concentrations were prepared by dilution with 0.8% NaCl solution, and 100 L of air (CO₂ content of 520 ppm) was bubbled through them at a rate of 10 L/min at 15°C. The results of measuring the HOCl emission from such solutions are given in Table 2 and Fig. 5.

As seen, when the initial NaOCl solution is diluted, the pH changes insignificantly; however, after bubbling air, it decreases, especially for the least concentrated solutions, due to a decrease in the buffer capacity. Nevertheless, there is an almost direct relationship between the concentration of total chlorine in solution and in air, and deviations from it are explained by a decrease in pH when air is bubbling through dilute solutions, which leads to an increase in the HOCl content in accordance with Fig. 2.

Influence of the temperature on HOCl emission process

The results of studying the HOCl emission from 100 mL of a NaOCl solution (1152 mg/L active chlorine, initial pH 9.50) at different temperatures during air (CO₂ content of 450 ppm) bubbling through it at a rate of 10 L/min for 50 min are shown in Table 3.

As expected, HOCl emission increases with increasing temperature, but this dependence is non-linear. The deviations are primarily due to different pH values of the solutions saturated with CO₂ during

Table 2
Emission of active chlorine into the air from solutions with different NaOCl concentrations

Dilution, stock NaOCl solution: water	Active chlorine concentration, mg/L	The initial pH of the working NaOCl solution	pH of the working NaOCl solution after air bubbling	The amount of active chlorine absorbed by the absorption solution, mg	Average concentration of active chlorine in the air (C_{AC}), mg/m ³
10:90	110	8.33	8.02	0.087	0.87
20:80	220	8.37	8.08	0.176	1.76
30:70	329	8.39	8.14	0.236	2.36
40:60	439	8.40	8.15	0.272	2.72
50:50	549	8.39	8.27	0.321	3.21
60:40	659	8.39	8.28	0.372	3.72
70:30	769	8.39	8.28	0.422	4.22
80:20	878	8.41	8.36	0.459	4.59
100:0	1098	8.42	8.42	0.584	5.84

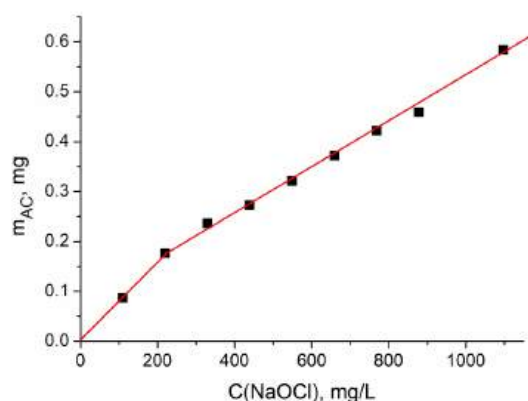


Fig. 5. Emission of total chlorine from NaOCl solutions of different concentrations

Table 3

Emission of HOCl into the air from NaOCl solution at different temperatures

Temperature, °C	pH of NaOCl solution after saturation with CO ₂	Average concentration of total chlorine in the air (C _{AC}), mg/m ³
15	8.41	5.89
20	8.48	6.82
25	8.58	8.75
30	8.83	11.64

the experiment, which is explained by a decrease in the solubility of CO₂ and HOCl with increasing temperature.

Influence of salinity on the HOCl emission process

The most common impurities in NaOCl solutions similar to those used in this study are sodium chloride, which is a raw material for its electrochemical synthesis. Thus, to study the effect of salinity on the HOCl emission, we used solutions prepared by adding different NaCl amounts to the base stock NaOCl solution. The results obtained during 50 min of bubbling 10 L/min of air (CO₂ content of 500 ppm) at 15°C through NaOCl solutions of 1160 mg/L active chlorine and 8 g/L, 16 g/L and 32 g/L NaCl showed that the average air total chlorine concentrations were 5.91, 6.32 and 6.55 mg/m³, respectively. The pH of the solution practically did not change with increasing NaCl concentration and remained within the range of 8.40–8.45 after saturation with CO₂. Thus, the increase in salinity has practically no effect on HOCl emission in comparison with the effect of pH and concentration of NaOCl working solution.

Conclusions

The developed method with the use of taurine as an absorbing solution allows reliably determining the low total chlorine concentrations in the gas phase. The data obtained indicate that, under the condition of a constant acidity of NaOCl solutions in the pH range of 5.50–11.50, the HOCl emission into the gas bubbled through the solution occurs gradually and evenly. Its amount in the air is strictly proportional to its content in the working NaOCl solution, which, in turn, can be calculated knowing the total chlorine concentration and using the known distribution diagrams of the mole fractions of active chlorine components at given pH. At least in the pH range of 7.50–8.45, NaOCl solutions are capable of maintaining a relatively constant level of HOCl emission into the air. Under the conditions organized by us, using an electrochemically synthesized 1100–1200 mg/L NaOCl solution, it is possible to reach the total chlorine concentration in the passing air flow up to 28 mg/m³, which guarantees rapid neutralization of any pathogens in it. The data obtained can be used by us to develop new types of systems for complex disinfection of premises.

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ВПЛИВ РІЗНИХ ФАКТОРІВ НА ВИДІЛЕННЯ ГІПОХЛОРИТНОЇ КИСЛОТИ З РОЗЧИНІВ ГІПОХЛОРИТУ НАТРІЮ В ПОВІТРЯ

Б. Мурашевич, Д. Гиренко, О. Лебідь, Г. Маслак, О. Нетроніна

Сполуки активного хлору є потужними мікробіцидними агентами, які традиційно використовуються для дезінфекції поверхонь. Після пандемії COVID-19 активно вивчається можливість використання цих сполук для обробки повітря з метою боротьби з поширенням інфекційних захворювань. Перспективним є створення систем дезінфекції, які б дозволяли підтримувати в повітрі приміщень достатню концентрацію найбільш ефективного газоподібного антимікробного компонента активного хлору – гіпохлоритної кислоти (HOCl). У даній роботі досліджено вплив різних факторів на процес виділення HOCl в повітря під час його барботування через розчини гіпохлориту натрію (NaOCl). Удосконалено колориметричний метод визначення вмісту загального хлору в повітрі. Досліджено вплив основних параметрів робочого розчину NaOCl на вміст HOCl у повітрі. Показано, що при постійному рН робочого розчину кількість загального хлору в повітрі строго пропорційна концентрації HOCl у розчині, яку, у свою чергу, можна розрахувати за відомими діаграмами молярного розподілу компонентів активного хлору. При використанні електрохімічно генерованих робочих розчинів NaOCl (з концентрацією приблизно 1100 мг/л за активним хлором) без додаткових корегувань складу можна підтримувати концентрацію HOCl в повітрі в межах 6,0–11,6 мг/м³. Отримані дані можуть бути використані при створенні установок для фумігаційної дезінфекції повітря приміщень та оцінці ризиків забруднення повітря хлорактивними сполуками.

Ключові слова: активний хлор, гіпохлоритна кислота, гіпохлорит натрію, газовиділення, дезінфекція.

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INFLUENCE OF VARIOUS FACTORS ON THE EMISSION OF HYPOCHLOROUS ACID FROM SODIUM HYPOCHLORITE SOLUTIONS INTO THE AIR

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Active chlorine compounds are powerful microbicidal agents traditionally used for surface disinfection. Following the COVID-19 pandemic, the potential use of these compounds for air treatment to mitigate the spread of infectious diseases has been actively studied. A promising approach involves developing disinfection systems capable of maintaining a sufficient concentration of the most effective gaseous antimicrobial component of active chlorine – hypochlorous acid (HOCl) – in indoor air. This study investigates the influence of various factors on the emission of HOCl into the air during its bubbling through sodium hypochlorite (NaOCl) solutions. A colorimetric method for determining the total chlorine content in the air has been refined. The effects of key parameters of NaOCl working solutions on the HOCl concentration in the air have been examined. It has been demonstrated that, at a constant pH of the working solution, the total chlorine content in the air is strictly proportional to the HOCl concentration in the solution, which, in turn, can be determined using established molar distribution diagrams of active chlorine species. When electrochemically generated NaOCl working solutions (containing approximately 1100 mg/L of active chlorine) are used without additional composition adjustments, the HOCl concentration in the air can be maintained within the range of 6.0–11.6 mg/m³. The findings of this study can be applied in the development of fumigation-based air disinfection systems and in the assessment of air contamination risks associated with chlorine-containing compounds.

Keywords: active chlorine; hypochlorous acid; sodium hypochlorite; gas emission; disinfection.

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