

Quantitative Spectrophotometric Methods for Determination of Sodium Hypochlorite in Aqueous Solutions

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Abstract □ Two simple spectrophotometric procedures for the quantitative estimation of hypochlorite in commercially available sodium hypochlorite solutions are presented. One method is based directly on the absorbance of hypochlorite in alkaline aqueous media. The other method takes advantage of the quantitative reaction of hypochlorite and ammonia in alkaline solution to form chloramine, which has a higher molar absorptivity. Results of the spectrophotometric assays are compared with results obtained by the titrimetric procedure of NF XII.

Keyphrases □ Sodium hypochlorite determination—aqueous solutions □ Chloramine determination—Na hypochlorite analysis □ Molar absorptivity—Na hypochlorite, chloramine □ UV spectrophotometry—analysis

Of the various methods available for quantitative determination of sodium hypochlorite in aqueous solution, most are the volumetric or gravimetric type (1-4). All of these methods are relatively laborious, time-consuming, and expensive to do on a routine basis. The method described in the NF XII, while giving good precision and accuracy, requires the preparation of several solutions, some of which must be standardized (1).

The purpose of this work was to develop procedures equally sensitive compared to the NF method, which could be used routinely for the quantitative determination of sodium hypochlorite. The facts that hypochlorite ion has an absorbance maximum at 292.5 $m\mu$ in alkaline aqueous solution (5) and that the absorbance shows a direct relationship to concentration of hypochlorite were utilized in one procedure. The other procedure is based on the quantitative reaction of hypochlorite with ammonia to yield chloramine (6), which has an absorbance maximum at 244.3 $m\mu$ that is also linearly related to concentration.

EXPERIMENTAL

Reagents—Commercially available sodium hypochlorite solutions were used. Hypochlorous acid solutions were prepared by the method of Higuchi *et al.* (7). Reagent grade ammonium hydroxide (58%) (Mallinckrodt) was diluted with distilled water to yield a 20% ammonium hydroxide solution. All water was distilled from acid permanganate solution in an all-glass still.

Spectrophotometric measurements were carried out using a Cary model 14 spectrophotometer. A Beckman pH meter was used for all pH measurements.

Procedures—*Spectral Changes of Hypochlorous Acid as a Function of pH*—Solutions containing 2.13×10^{-3} *M* hypochlorous acid at various pH values were prepared. The spectral changes were determined by examining the UV spectra from 400 to 250 $m\mu$.

Standardization of Hypochlorous Acid Solutions—A suitable volume (3 ml.) of hypochlorous acid solution at 25° was pipeted into a stoppered conical flask and diluted with about 100 ml. of water. One milliliter of glacial acetic acid and 2 g. of potassium

iodide were then added, and the stoppered flask was placed in the dark for 5-10 min. The liberated iodine was then titrated with standard sodium thiosulfate solution, using 1 ml. of starch solution as an indicator.

Iodometric Determinations of Sodium Hypochlorite—These determinations were carried out according to a modification of the procedure described in NF XII. The modification consisted of pipeting 3 ml. of the sample at 25° rather than weighing it.

Spectrophotometric Method I—The molar absorptivity of hypochlorite was determined as follows. Solutions containing concentrations ranging from 8.73×10^{-4} to 34.92×10^{-4} *M* sodium hypochlorite were prepared by pipeting 1, 2, 3, and 4 ml. of a standardized hypochlorous acid solution into 100-ml. volumetric flasks. Two milliliters of 10% sodium hydroxide solution and 75 ml. of distilled water were then added to each flask, and the solutions were allowed to equilibrate at 25°. After equilibrating, the solutions were brought to volume with distilled water at 25°. A plot of the absorbance of each solution in a 1-cm. stoppered cell at 292.5 $m\mu$ versus concentration was used to calculate the molar absorptivity of hypochlorite ion.

The hypochlorite content of commercial bleaches was determined by pipeting 1 ml. of bleach at 25° into a 200-ml. volumetric flask and adding 175 ml. of water and 1 ml. of 10% sodium hydroxide solution. The solution was then equilibrated at 25° and brought to volume with distilled water of the same temperature. Its absorbance at 292.5 $m\mu$ was then determined against a similarly prepared solution containing no bleach. Using the molar absorptivity and a molecular weight at 74.5 g./mole for sodium hypochlorite, the concentration of sodium hypochlorite (in mg./ml.) of bleach solution was calculated.

Spectrophotometric Method II—The molar absorptivity of chloramine was determined by preparing concentrations of chloramine varying from 8.73×10^{-4} to 34.92×10^{-4} *M*. This was done by pipeting 1, 2, 3, and 4 ml. of a standardized hypochlorous acid solution (at 25°) into four 100-ml. volumetric flasks, followed by addition of about 75 ml. of distilled water and 2 ml. of 10% sodium hydroxide solution. The flasks were then equilibrated at 25° in a water bath. To one of the solutions was added 2 ml. of 20% ammonium hydroxide, and the solution was brought to volume with distilled water. The absorbance was measured immediately at 244.3 $m\mu$ in a 1-cm. stoppered cell using a suitable blank. Each of the remaining solutions was treated in an identical way. A plot of absorbance versus concentration was made, and the molar absorptivity was calculated.

Determination of hypochlorite content of commercial bleaches was made by pipeting 1 ml. of bleach at 25° into a 200-ml. volumetric flask. The sample was diluted with 175 ml. of distilled water and 1 ml. of 10% sodium hydroxide solution. The resulting solution was equilibrated at 25°. Two milliliters of 20% ammonium hydroxide solution was then added to the flask, and distilled water was added to bring the solution to a volume of 200 ml. The absorbance was then immediately measured at 244.3 $m\mu$ against a blank which was prepared in the same way except the bleach was omitted.

DISCUSSION

Spectrophotometric Method I—Since this method was based on the absorbance-concentration relationship of hypochlorite ion, it was necessary to determine the minimum pH required to ensure that all hypochlorous acid was converted to hypochlorite ion. Therefore, several solutions containing identical amounts of hypochlorous acid were adjusted to various pH values, and their

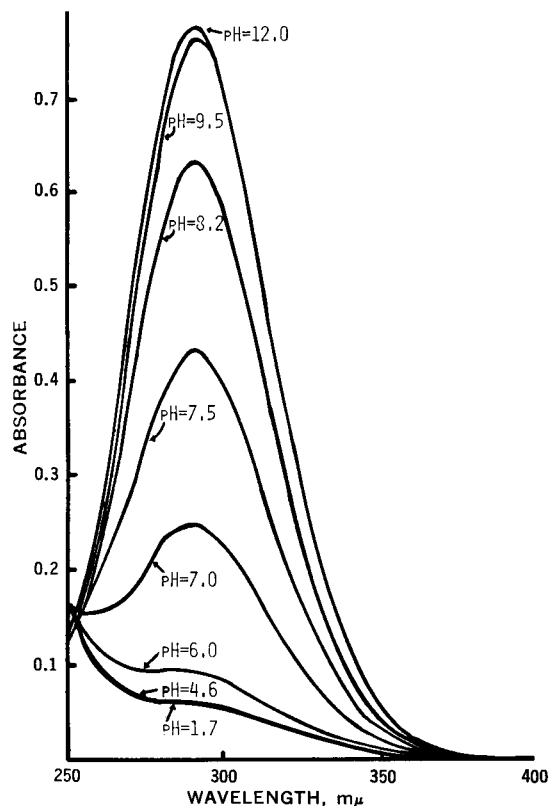


Figure 1—UV spectral changes of 2.13×10^{-3} M hypochlorous acid solutions as a function of pH. λ_{\max} is 292.5 μ .

spectra were obtained by scanning from 400 to 250 μ . It was found that at pH > 10, all hypochlorous acid had been converted to the hypochlorite ion. These data are shown in Fig. 1. All solutions subsequently used in the determination of the absorptivity and in analysis of hypochlorite were made such that pH > 10.

From Fig. 1, it was also determined that $\lambda_{\max} = 292.5$. When absorbance at λ_{\max} was plotted against pH (Fig. 2), a typical sigmoid-shaped curve was obtained. From Fig. 2, the pKa of hypochlorous acid was found to be 7.50, which agrees well with the value of 7.53 previously reported (8).

When the absorbance values at 292.5 μ of a series of hypochlorite solutions were plotted against their concentrations, a linear relationship was found. From these data the molar absorptivity was calculated ($\epsilon = 360 \pm 2 M^{-1} \text{ cm}^{-1}$).

The quantitative determination of hypochlorite in commercial bleach solution was done by pipeting a 1-ml. sample at 25° into a 200-ml. volumetric flask, adding excess alkali, and bringing to volume with water at 25°. The absorbance of the diluted solution was measured at 292.5 μ against a blank. The concentration in milligrams of sodium hypochlorite per milliliter of bleach was calculated according to the following equation:

$$\text{mg. of NaOCl/ml. of bleach} = A \times MW \times V_D / \epsilon V_S \quad (\text{Eq. 1})$$

where: A = absorbance at 292.5 μ
 ϵ = molar absorptivity of hypochlorite (at 292.5 μ)
 $= 360 M^{-1} \text{ cm}^{-1}$
 MW = molecular weight of NaOCl = 74.5
 V_D = total volume of diluted solution (in ml.)
 V_S = volume of bleach sample solution used (in ml.)

The stability of the solutions was checked, and no change in absorbance at 292.5 μ was observed over a 2-hr. period.

Spectrophotometric Method II—An earlier report (6) has shown that hypochlorous acid in alkaline solution reacts rapidly in the presence of excess ammonia to form chloramine quantitatively according to the following scheme: $\text{NH}_3 + \text{HOCl} \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$.

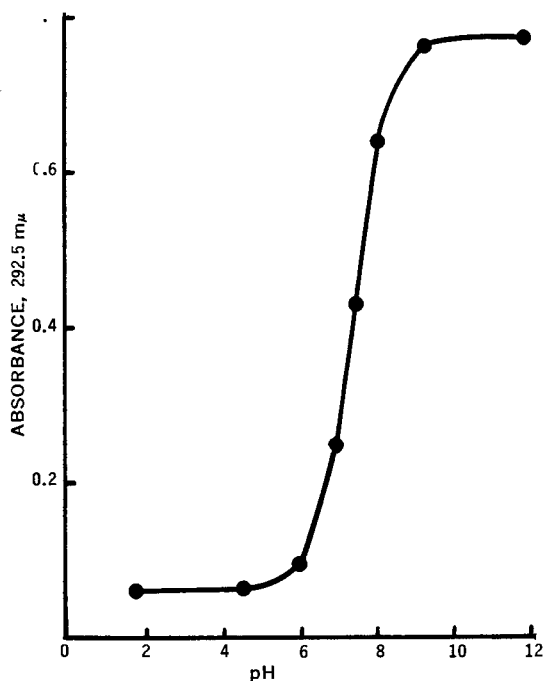


Figure 2—Absorbance at 292.5 μ of 2.13×10^{-3} M hypochlorous acid solutions as a function of pH.

This information was used as the basis for the indirect determination of hypochlorite. Figure 3 shows the difference in spectra between hypochlorite solution at pH > 10 and a similar solution to which excess ammonia has been added to form chloramine. The λ_{\max} shifted from 292.5 μ for hypochlorite to 244.3 μ for chloramine. When various concentrations of hypochlorous acid were treated with ammonium hydroxide at pH > 10, and the absorbance at 244.3 was plotted against the concentration of chloramine (which is equimolar with hypochlorite), a linear relationship was observed. From the slope of the line, the molar absorptivity was calculated to be $459 \pm 3 M^{-1} \text{ cm}^{-1}$. Actual determinations of sodium hypochlorite in commercial bleach samples were similarly

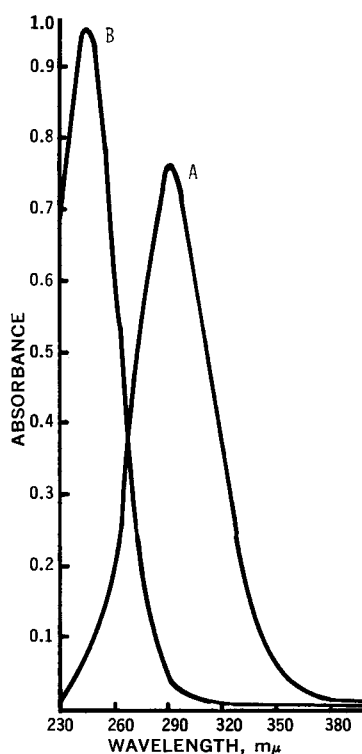


Figure 3—Spectra of 2.1×10^{-3} M solutions of (A) hypochlorite and (B) chloramine (formed by addition of ammonium hydroxide to hypochlorite solutions).

Table I—Results and Comparisons of Hypochlorite Assay of Three Commercial Bleaches at 25°. Results Expressed as Milligrams of Sodium Hypochlorite per Milliliter of Bleach

Bleach Solution	Assay Method	Number of Determinations	Range of Results, mg./ml.	Mean and Standard Deviation, mg./ml.
1	NF ^a	5	39.5–40.3	39.8 ± 0.3
1	Spectrophotometric method I ^b	5	39.6–39.8	39.6 ± 0.1
1	Spectrophotometric method II ^c	5	39.5–39.8	39.7 ± 0.1
2	NF ^a	7	15.1–15.4	15.2 ± 0.2
2	Spectrophotometric method I ^b	7	15.3–15.4	15.3 ± 0.1
2	Spectrophotometric method II ^c	7	15.0–15.1	15.1 ± 0.1
3	NF ^a	5	59.7–60.2	59.7 ± 0.2
3	Spectrophotometric method I ^b	5	60.0–60.3	60.1 ± 0.2
3	Spectrophotometric method II ^c	5	59.1–59.5	59.3 ± 0.2

^a Used volume at 25° rather than weighing sample in NF assay. ^b Measured as hypochlorite at 292.5 m μ . ^c Measured as chloramine at 244.3 m μ .

carried out, and the concentration of sodium hypochlorite in milligrams per milliliter of bleach was calculated according to Eq. 1 where now A = absorbance of chloramine at 244.3 m μ , and ϵ = molar absorptivity of chloramine = 459 M⁻¹ cm.⁻¹.

When the absorbance of chloramine solutions was observed over a period of time, no significant changes were seen in 4–5 min. However, 1–2% decreases in absorbance were observed after 30 min. To minimize the experimental error due to the instability of chloramine, all solutions were prepared up to the point where the ammonium hydroxide was to be added. At this point, one solution at a time was taken and to it were added the ammonium hydroxide and distilled water to bring it to volume. The absorbance was then immediately measured.

RESULTS AND CONCLUSIONS

The hypochlorite content of three different bleach solutions was determined by the NF method and the two spectrophotometric methods; the results are shown in Table I. The results obtained for each sample are in good agreement for all three analytical methods.

The simplicity and ease of the spectrophotometric methods as opposed to the NF method would seem to suggest the former as the methods of choice in the determination of hypochlorite in aqueous solution. In addition, the spectrophotometric methods allow for analysis of much more dilute solutions than the NF method. For example, if a 10-cm. cell and the expanded scale of the Cary 14 spectrophotometer were used, concentrations as low as several micrograms per milliliter could be determined. This could be extremely useful, especially when applied to the determination of active chlorine in water.

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