



ORIGINAL RESEARCH ARTICLE

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STUDY ON DETERMINATION OF FREE CHLORINE CONTENT IN SODIUM DICHLOROISOCYANURATE SOLUTION BY UV-Vis ABSORPTION SPECTROMETRY

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ABSTRACT

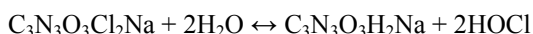
The study presents experimental results determining the free chlorine content by UV-Vis absorption spectrophotometry using a calibration curve with the standard solution NaOCl. The chlorine in exists an aqueous solution as HOCl and OCl⁻ depending on pH of media, that are known as free chlorine. The maximum absorption wavelengths of OCl⁻ and HOCl in aqueous media formed from sodium hypochlorite are 291 and 292 respectively. Based on these wavelengths OCl⁻ and HOCl content might be determined using UV-Vis absorption spectrophotometric method resulted in good data.

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INTRODUCTION

As known, generally, in aqueous media, sodium dichloroisocyanurate (NaDCC) is hydrolyzed to form hypochlorous acid HOCl and sodium cyanurate as following



However, not all chlorine content in NaDCC hydrolyzes into HOCl. According to the author (Lâm Ngọc Thu, 2005; Kuznesof, 2003; Pinto and Rohrig, 2003) the free chlorine of pure NaDCC is 64.5% and of dihydrate NaDCC is 55.5%. Thus a part of chlorine still exists in NaDCC called bound available chlorine (Qiang Wang et al., 2011; Thomas Clasena, Paul Edmondson, 2006; Fawell, 2007; Adam and Gilbert Gordon, 1999). The sodium dichloroisocyanurate (NaDCC) is hydrolyzed to produce HOCl and depending on pH and then HOCl proceeds to hydrolyze to form OCl⁻. Free chlorine exists in the form of HOCl and OCl⁻ in solution and are capable of taking part in the oxidation of organic compounds. Bound available chlorine exists in association with other substances or in NaDCC and can be hydrolyzed to form

free chlorine, which is not capable of reacting as the specific reactions of HOCl and OCl⁻. In solution of NaDCC total active chlorine content is the sum of free chlorine and bound available chlorine. In the process of hydrolysis of NaDCC, the active chlorine content exists in both free chlorine and bound chlorine. When free chlorine takes part in oxidation reactions with an organic compound, the equilibrium state of the hydrolysis process in solution is changed, the bound chlorine is immediately hydrolyzed to form free chlorine, to proceed the oxidation process. The new equilibrium is established between free chlorine and the various chloroisocyanurates. When hypochlorous acid is consumed for an oxidation reaction, the chloroisocyanurates will rapidly dissociate to release more hypochlorous acid. There are many methods for determining the free chlorine content in NaDCC solution such as High Performance Liquid Chromatography (HPLC), Gas Chromatography (GC), Gas Chromatography/Mass Spectrometry (GC/MS), UV-Vis Spectrophotometry. However UV-Vis absorption spectrometry is more suitable in analyzing free chlorine in solution. Due to this reason, in this paper this method is used to determine free chlorine content in solution.

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EXPERIMENTAL

Apparatus and Chemicals

Apparatus: UV-Vis Spectrophotometer UV-VIs Jasco V530, Japan

Chemicals: Sodium dichloroisocyanurate (Sigma - Aldrich); Solution NaOCl 10% Vietnamese Chemical Company; Chloramine B, BOCHEMIE, sro, Lidická 326, 735 95 Bohumin, Czech Republic)

NaOH, Na₂SO₄, Na₂HPO₄, HCl, Merck.

Experimental procedure

Building up standard plot

Preparation of standard solutions

Take 10 mL of NaOCl solution into a conical flask containing 50 mL of distilled water. The NaOCl concentration was determined using titration method with KI reagent as described in [4,6]. Take 2 mL of the prepared standard solution, add 6 mL of 0.01M NaOH or 6 mL of 0.01M HCl to obtain a different pH solution. Noted solution S1(with NaOH) and solution S2 (with HCl). Take 1 mL of standard solution from solution S1 and S2 diluted with 1, 3, 5, 7, 10 mL of distilled water before measuring absorbance in the range from 200 to 700 nm. The maximum absorbance of each solution from S1 and S2 was used for building up standard plot.

Determining Limit of detection (LOD, Limit of quantitation (LOQ) and Recovery rate: The LOD, LOQ, the recovery rate (H) were determined by the method of calculating the result of the standard addition of the sample to the blank sample with low concentration (Lâm Ngọc Thu, 2005).

Take a blank sample: 6 mL of twice distilled water

Standard addition sample: Take 02 mL of standard solution. The experiments were repeated n times.

* The LOD value was calculated as following:

$$\text{LOD} = t_{\alpha}(n) * \text{SD}$$

Here $t_{\alpha}(n)$ T- student, chosen $n=10$, $\alpha=0,005$ then resulted in $t_{\alpha}(n)=3,169$

C_{tb}: mean value of blank sample $C_{tb} = \frac{\sum C_i}{n}$

SD: Standard derivation $SD = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (C_i - C_{tb})^2}$

* Limit of quantitation (LOQ) was calculated by the expression:

$$\text{LOQ} = 10 * \text{SD}$$

* Permissible limits for repeatability $\text{RSD} = \text{SD}/C_{tb}$

* Recovery rate H: The measurement was repeated three times n then calculated by the following expression:

$$H = \frac{F - I}{A} * 100\%$$

Here: F is concentration of sample with standard addition; I is concentration of sample;

A is concentration of theoretical analyte concentration.

* The measurement permissible is when:

$$\text{For } \text{RSD} < \frac{1}{2} * \text{RSDr (Horwitz) (\%)} = C^{-0,1505}$$

C is target analyte.

$$\text{For } \text{LOD} \leq C_{\text{spike}} \leq 10 \text{ LOD}, 2,5 \leq (C_{\text{tb}}/\text{SD}) \leq 10$$

$$\text{For } 85\% \leq H \leq 115\%$$

Determination of free chlorine content: Weigh 0.6 g of NaDCC diluted in 100 mL distilled water at 27°C to obtain solution S3. Take 3 mL of solution S3, add 3 mL of NaOH 0.01 M or 3 mL of HCl 0.01 M to form a solution of NaDCC at different pH, obtain solution S4 and solution S5 and measure absorbance. The free chlorine in the solution S4 and S5 was determined based on the standard plot.

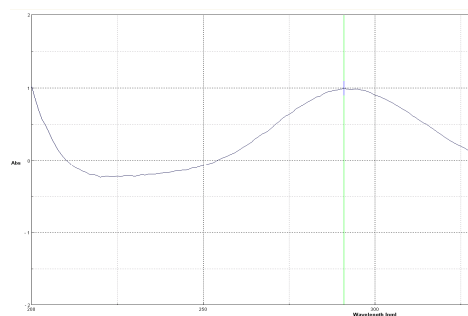
RESULT AND DISCUSSION

The maximum absorbance of free chlorine

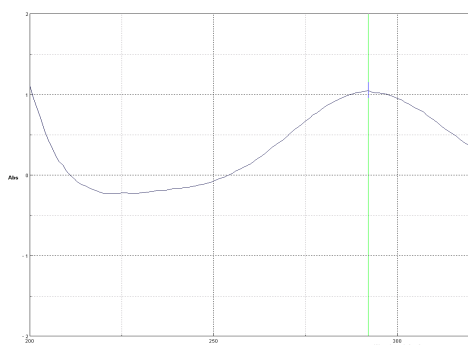
The maximum absorbance of free chlorine at different pH was represented in Table 1 and in Figure 1.

Table1. The maximum absorption wavelength of free chlorine

Nr.	Sample	Free chlorine conc. (mM)	pH	Maximum λ_{max} (nm)
1	S 1	5.42	11.32	291
2	S 2	5.42	4.17	292



a. Absorption of free chlorine in S1



b. Absorption of free chlorine in S2

Fig.1. UV-Vis spectrophotometry curves of free chlorine in samples

The Table 1 and Figure 1. Showed that:

Free chlorine in NaOCl solution has exhibited the maximum absorbance at two different wavelengths depending on the pH of the NaOCl solution. However, the level of change is very small (01 nm). The peak absorption peak of S1 (pH > 7) and S2 (pH < 7) are both clear and distinct. The maximum absorption wavelength at λ_{max} of 291, 292 nm can be used to analyze the free chlorine content.

Standard plot

The absorbance range of free chlorine with different concentrations at maximum absorption wavelengths of 291 and 292 nm on the Jasco V530 UV-Vis was represented in Figure 2.

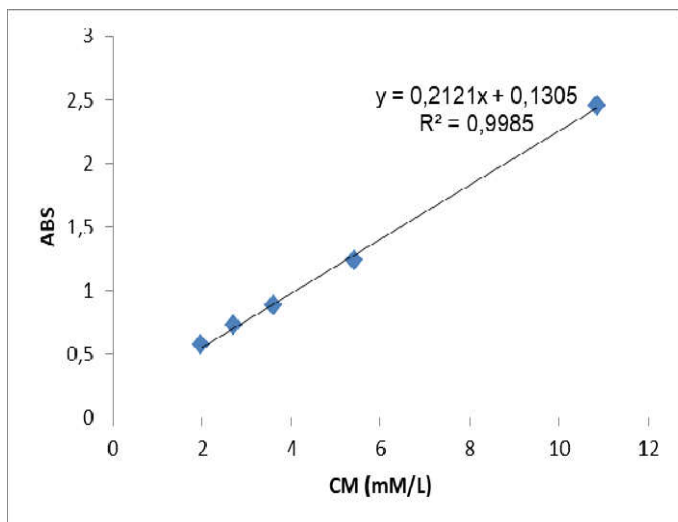


Fig. 2. The standard plot of free chlorine in the concentration range from 1.97 to 10.84 mM

Results of analyzing the Limit of detection, limit of quantitation and recovery

Measure the absorbance of the standard sample added with a certain concentration of analyte, (free chlorine content), based on the calibration curve set out in section 3.2 to determine the free chlorine content in this sample. Statistical calculations according to Section 2.2.2 yield results in Table 2.

Table 2. Statistical values of the method of determining the free chlorine content in the solution

Blank sample	Samples added with standard conc.	C(mM) HOCl	Statistical values					
			C _{tb}	SD	LOD	LOQ	RSD	H%
Distilled water	Standard conc (C _{TC} = 3.61 mM)	3.78	3.63	0.388	1.229	3.880	0.107	100.66
		3.69						
		3.44						
		3.47						
		3.68						
		3.81						
		3.21						
		3.52						
		3.82						
		3.92						

From data present in Table 2 the following findings are obtained:

- Permissible limits for repeatability :

$$RSD = 0,107 < \frac{1}{2} * RSDr \text{ (Horwitz) } (\%) = C^{-0,1505} = 0,8243$$

C is concentration in the test sample.

- Limit of detection LOD:

$$LOD = 1,229 \leq C_{spike} = 3,61 \leq 10 LOD = 12,29$$

$$2,5 \leq (C_{tb}/SD) = 9,366 \leq 10$$

- Recovery H, %:

$$85\% \leq H = 100, 66\% \leq 115\%$$

Thus, the method of analysis was suitably applied to determine free chlorine content with the detection limit of 1.23 mM / L, limit of quantitation of 3.88 mM / L, a relative standard deviation of 0.107 and the recovery rate of 100.66%. The method can be used to analyze free chlorine content in solution.

Determination of free chlorine content in NaDCC solution

Determination of free chlorine content according to item 2.2.3, the results are shown in Table 3.

- It is possible to determine the free chlorine content in NaDCC solution using the UV-Vis Jasco V530.
- The free chlorine content in NaDCC solution at different pH is different. This is closed to the published research (Kuznesof, 2003).

Conclusion

From the results of the study it can draw the following conclusions:

- Free chlorine exhibits two maximum absorption wavelengths at 291 nm at pH 11.32 and 292 nm at pH 4.17.
- The free chlorine content in the solution of NaDCC can be determined by UV/Vis absorption spectrophotometry method at two wavelengths of maximum absorption at 291 and 292 nm on the Jasco

Table 3. The free chlorine content in solution of NaDCC

Parameters	Solution S 4	Solution S 5
pH	11.54	4.52
Conc. NaDCC (mM/L)	13.63	13.63
Free chlorine conc. (mM/L)	7.27	6.42

V530 UV-Vis device with the correlation coefficient $R^2 = 0.9985$.

- LOD of free chlorine content was limited to 1.23 mM, LOQ was 3.880 mM and the relative standard deviation was 0.107, the recovery was 100.66 %
- Based on the calibration curve, the free chlorine content in NaDCC solution was 13.63 mM, 7.27 mM, at pH = 11.54 and 6.42 mM, respectively at pH = 4.52.

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