

NEW SPECTROPHOTOMETRIC METHOD WITH KMnO_4 FOR DETERMINATION OF HYPOCHLORITE IN COMMERCIAL BLEACHES

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(Received November 13, 2003; August 13, 2004)

ABSTRACT. Hypochlorite with a strong germicidal and bleaching action forms the active component in most commercial bleaches. The new method, an instrument-based and simple experimental procedure involves the reaction of the hypochlorite with arsenious oxide (As_2O_3) (pH 6.5) followed by the coupled reaction of residual As_2O_3 with permanganate at acidic pH. A titration procedure is described and spectrophotometric method is designed using four ranges of calibration curves to enable the determination of hypochlorite in the range 2.5×10^{-4} to 2.4×10^{-2} M from the KMnO_4 absorbance measurements. A series of commercial bleaches are tested using the proposed spectrophotometric method. The results proved more precise and accurate than by arsenite method.

KEY WORDS: Commercial bleaches, Hypochlorite determination, Spectrophotometric method

INTRODUCTION

Sodium hypochlorite is one of the most versatile chemicals to which we are constantly exposed. It is a powerful oxidizing agent, disinfectant and deodorizer [1, 2]. It effectively destroys disease-causing bacteria [3]. Due to the abundance of its applications, hypochlorite is used in households, industries, hospitals and laboratories and in treatment of effluent [4]. Several methods including kinetics based have been reported in literature for the OCl^- determination [5-9]. Some of these, being titrimetric in nature and with internal or external indicators, are prone to human error [5-7]. Most widely used method is titrimetric method using arsenite and KI paper as an external indicator [6, 7]. The need for a simple, quick and reliable method for its accurate determination has stirred interest and is the focus of this paper.

EXPERIMENTAL

All experiments were performed using double distilled water and reagents of analytical grade or high purity. All glassware was thoroughly cleaned, rinsed with distilled water and dried before use.

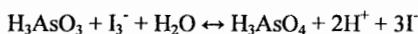
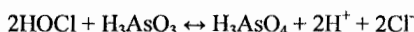
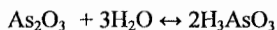
Arsenious oxide standard solution

A 0.025 M As_2O_3 stock solution was prepared by dissolving 2.473 g finely powdered arsenious oxide in a 10% w/v sodium hydroxide solution. The solution was diluted to 200 mL and neutralized with 1 M hydrochloric acid. The neutralized solution was quantitatively transferred to a 500 mL volumetric flask. 2.0 g of pure NaHCO_3 was added and when all the salt was dissolved, the solution was made up to the mark [5].

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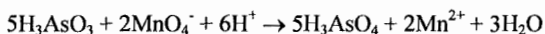
Preparation and standardization of hypochlorite

Sodium hypochlorite solutions were prepared by electrolysis of sodium chloride solutions using the Baird and Tatlock Electrolytic Analysis Apparatus [9, 10]. On optimizing operating conditions for OCl^- generation, it was found that a 5% NaCl solution refrigerated for 1 h and electrolyzed at 2 amperes (A) for 45 min produced $[\text{OCl}^-]$ of approximately 2.8×10^{-3} M. The generated hypochlorite solutions were stored in brown bottles away from light to minimize decomposition caused by light and air. The OCl^- solutions were standardized according to the arsenite method, i.e. reacting known amount of arsenite with hypochlorite and titrating the excess arsenite with standard iodine solution [5, 9]. The chemistry of the reaction can be summarized as follows [5]:



The reaction between arsenite (arsenous acid) and iodine is reversible one and proceeds quantitatively from left to right, if the hydrogen iodide is removed from the solution as fast as it is formed. This can be achieved by the addition of sodium bicarbonate. Optimum pH for complete oxidation of arsenite is reported to be 6.5 [5].

A stock solution of permanganate (approximately. 0.02 M, 1 L) was prepared by dissolving about 3.25 g KMnO_4 to 1.0 L water. The beaker containing the permanganate solution covered with clock glass was gently boiled for 15 – 20 min. The solution, once cooled to the lab temperature, was filtered through porcelain filtering crucible. The permanganate solutions were daily standardized as follows: To 25.0 mL of standard As_2O_3 solution, 100 mL H_2O , one drop of 2.50×10^{-3} M KI (acts as catalyst) and 10.0 mL concentrated hydrochloric acid were added. The resulting solution was titrated with the KMnO_4 to the pale permanent pink indicating marginal excess of the oxidant. Acidic pH facilitates the oxidation by permanganate resulting in sharp end point.



A Cary II – Double beam spectrophotometer with data capturing facilities interfaced with a PC was used where necessary, to measure the absorbance (at 525 nm) corresponding to permanganate. The Microsoft-Excel software was used for the statistical analysis, i.e. the t and f tests on the analytical data.

RESULTS AND DISCUSSION*Titration experiments*

Keeping the total volume 10.0 mL, various aliquots of a 2.50×10^{-2} M OCl^- stock were added to 1.25×10^{-2} M (5 mL of 2.5×10^{-2} M) As_2O_3 . After reaction time of one minute, 1 mL of 5.0 M H_2SO_4 and 1 mL of 1.0×10^{-6} M KI were added. The reaction mixture was then titrated with the standard KMnO_4 to pale permanent pink. The titration experiments were performed in triplicate and the average titration values were recorded. All standard deviations are ≤ 0.1 mL, indicating good precision and reproducibility of the titration values. Table 1 summarises the mean analytical results obtained from the triplicate titration experiments.

Table 1. Titration values for the $\text{OCl}^- - \text{As}_2\text{O}_3 - \text{KMnO}_4$ method.

$[\text{OCl}^-] = 2.50 \times 10^{-4} - 2.50 \times 10^{-2} \text{ M}$, $[\text{KI}] = 1.0 \times 10^{-7} \text{ M}$, $[\text{As}_2\text{O}_3] = 1.25 \times 10^{-2} \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.50 \text{ M}$, $[\text{KMnO}_4] = 2.50 \times 10^{-3} \text{ M}$

$[\text{OCl}^-]$ (M)	Vol. of KMnO_4 mL*	s	CV (%)	Estimated $[\text{OCl}^-]$ (M)
2.50×10^{-4}	19.93	0.09	0.45	2.446×10^{-4}
2.50×10^{-3}	18.22	0.07	0.38	2.389×10^{-3}
5.0×10^{-3}	16.10	0.10	0.62	5.048×10^{-3}
6.25×10^{-3}	14.97	0.06	0.40	6.465×10^{-3}
1.0×10^{-2}	12.17	0.06	0.49	0.998×10^{-2}
1.25×10^{-2}	10.27	0.06	0.58	1.236×10^{-2}
1.50×10^{-2}	8.20	0.00	0.0	1.496×10^{-2}
1.88×10^{-2}	5.17	0.06	1.16	1.876×10^{-2}
2.25×10^{-2}	2.10	0.00	0.00	2.260×10^{-2}
2.50×10^{-2}	0.20	0.00	0.00	2.499×10^{-2}

*Mean of triplicate experiments, s = standard deviation and CV = coefficient of variation.

t-test: Two-sample assuming unequal variances.

Null hypothesis: There is no significant difference between the actual and estimated observations.

Observations = 10; t-critical = 1.73, t-stat = 0.000259, variance = 7.21×10^{-5} and probability = 0.9998.

The stoichiometric ratios of $\text{OCl}^-:\text{As}_2\text{O}_3$ and $\text{KMnO}_4:\text{As}_2\text{O}_3$ are 2:1 and 1:1.25, respectively [5, 7]. Knowing the initial number moles of As_2O_3 and the moles of KMnO_4 reacted with the residual excess of As_2O_3 solution, the moles of OCl^- reacted with As_2O_3 and its concentration can be calculated. It is obvious that with the proposed method involving the back titration of residual arsenite with permanganate, the hypochlorite concentration can be determined. The titration of residual arsenite with permanganate, which gives a sharp end point, needs no indicator. It is an improvement over the arsenite method that needs an external indicator. The plot of the permanganate titre volumes *versus* [hypochlorite] gave good straight line and the linear regression equation is represented $y = -797.35 x + 20.125$ with $R^2 = 0.9998$. The estimated concentrations using the linear regression curve are summarized in the last column of Table 1. t-Test is conducted using the expected and estimated hypochlorite values. With the null hypothesis that there is no significant difference between the actual and estimated observations and assuming the unequal variance, the t-test was conducted. With observations = 10, a t-stat value (2.59×10^{-4}) lower than the t-critical = 1.73, very low variance value (7.21×10^{-5}) and high probability value (0.999) support the hypothesis. Thus, the results are precise and reproducible.

As the aim of the study was to develop an instrument based method with improved accuracy, the back titration reaction method was transformed into a spectrophotometric method. Instead of titrating the residual arsenite with permanganate, a procedure of addition of fixed 5.0 mL aliquots of KMnO_4 solution to the mixture containing residual arsenite was designed till a permanent pink colour is noticed in the mixture.

The titration results allow the splitting up of the hypochlorite concentrations into four ranges. In the 1st range with high concentration of hypochlorite, i.e. $2.50 \times 10^{-2} - 1.88 \times 10^{-2} \text{ M OCl}^-$, requiring zero to 5.0 mL of $2.50 \times 10^{-3} \text{ M KMnO}_4$ to completely consume the remaining arsenite, and for the 2nd range: $1.88 \times 10^{-2} - 1.25 \times 10^{-2} \text{ M OCl}^-$, 10.0 mL KMnO_4 was required. The 3rd range $1.25 \times 10^{-2} - 6.25 \times 10^{-3} \text{ M OCl}^-$, required about 15.0 mL KMnO_4 and finally the 4th range, with low 6.25×10^{-3} to $2.50 \times 10^{-4} \text{ M OCl}^-$ concentration required 20.0 mL of the KMnO_4 stock solution.

Calibration curves

Keeping sample plus water volume 5.0 mL, various concentrations of OCl^- were reacted with 5.0 mL of 2.5×10^{-2} M As_2O_3 . After 1 min, 1 mL each of 5.0 M H_2SO_4 and 1.0×10^{-6} M KI were added. Immediately, necessary volumes of (5, 10, 15 or 20 mL in 5.0 mL aliquots) of 2.50×10^{-3} M KMnO_4 were added to the reaction mixture till permanent pink colour is observed. After thorough mixing, the absorbance values at 525 nm were recorded. Table 2 summarises the typical absorbance values mean of triplicate runs after addition of 5.0 mL of permanganate (curve 1). The standard deviation and coefficient of variation were calculated as measures of precision for each set of absorbance values.

Table 2. KMnO_4 absorbance values for calibration curve 1.

{ $[\text{OCl}^-] = 1.88 \times 10^{-2} - 2.35 \times 10^{-2}$ M; $[\text{H}_2\text{SO}_4] = 0.50$ M (1.0 mL of 5.0 M); $[\text{As}_2\text{O}_3] = 1.25 \times 10^{-2}$ M (5 mL of 2.5×10^{-2} M); $[\text{KI}] = 1.0 \times 10^{-7}$ M (1.0 mL of 10^{-6} M); total volume = 10.0 mL plus $[\text{KMnO}_4] = 2.50 \times 10^{-3}$ M (5.0 mL)}

$[\text{OCl}^-] / 10^{-2}$ M	Residual Abs. at 525 nm	s	CV / %
1.88	0.0645	0.0005	0.78
1.95	0.2257	0.0006	0.26
2.05	0.3612	0.0007	0.19
2.15	0.5853	0.0007	0.12
2.25	0.8019	0.0004	0.05
2.35	0.9606	0.0006	0.06

s = standard deviation and CV = coefficient of variation.

Four calibration curves (mean absorbance versus $[\text{OCl}^-]$) were plotted using the four hypochlorite concentration ranges. The objective of four calibration curves was to increase sensitivity of the method and to broaden the range for hypochlorite determination. For the 1st range of 2.50×10^{-2} to 1.88×10^{-2} M OCl^- 5.0 mL permanganate, for the 2nd range 1.88×10^{-2} to 1.25×10^{-2} M range OCl^- 10 mL permanganate, for the 3rd range 1.25×10^{-2} to 6.25×10^{-3} M OCl^- 15 mL permanganate, and finally for the 4th range of 6.25×10^{-3} to 2.50×10^{-4} M OCl^- 20 mL permanganate were added. Total reaction time for a sample was less than 4 min and total volume changes due to addition of varied amounts of permanganate were taken into consideration in calculations.

Figure 1 illustrates the four calibration curves obtained with addition 5.0 mL (curve 1), 10.0 mL (curve 2), 15 mL (curve 3), and 20.0 mL (curve 4) of permanganate, respectively. According to the calibration curves for the OCl^- - As_2O_3 - KMnO_4 method the linear equations obtained are as follows:

Calibration curve 1: $y = 1.8372x - 0.2977$; 5.0 mL KMnO_4 added

Calibration curve 2: $y = 1.8053x - 1.3149$; 10.0 mL KMnO_4 added

Calibration curve 3: $y = 1.8002x - 2.4267$; 15.0 mL KMnO_4 added, and

Calibration curve 4: $y = 1.9197x - 3.5412$; 20.0 mL KMnO_4 added

The R^2 values that indicate the linear relationship between two variables were between 0.9941 and 0.9978 for all curves indicating that the calibration curves are good straight lines and confirming the reliability of the method over the range: 2.5×10^{-4} to 2.50×10^{-2} M. With the chosen initial As_2O_3 concentration (5 mL of 2.50×10^{-2} M), the combination of the four

calibration curves will enable the determination of $[\text{OCl}^-]$ over the range: 1.88×10^{-3} to 2.35×10^{-2} M. If necessary, with increased initial concentration of arsenite, the higher limit for the analysis range is extendable.

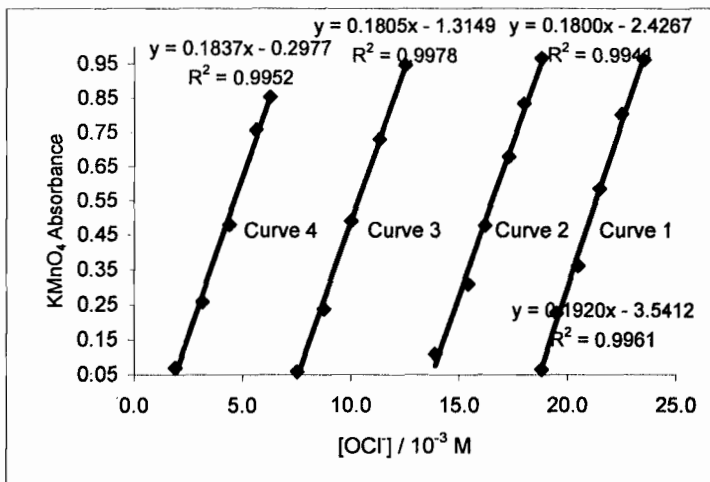


Figure 1. Combination of four calibration curves. $[\text{KMnO}_4]_0 = 2.50 \times 10^{-3}$ M, Volume of KMnO_4 : 5 mL = Curve 1, 10 mL = Curve 2, 15 mL = Curve 3 and 20 mL = Curve 4. Conditions same as in Table 2.

The low coefficients of variance indicate the excellent precision and reproducibility of results (Table 2). Further, t-tests were conducted on the expected and obtained values for each of the four calibration curves. Again, the hypothesis that there is no significant difference between the actual and estimated observations was used. The results obtained are summarized in Table 3. For all four curves the low t-stat values compared to the t-critical coupled with high probability values confirm the correctness of the hypothesis.

Table 3. Comparison of results: arsenite versus photometric methods.

{For photometric method, volume of bleach reacted = 5.0 mL, $[\text{As}_2\text{O}_3] = 1.25 \times 10^{-3}$ M; $[\text{H}_2\text{SO}_4] = 0.50$ M; $[\text{KI}] = 1.0 \times 10^{-7}$ M and $\text{KMnO}_4 = 20.0$ mL of 2.50×10^{-3} M; Figure 2, Curve 4 used}

Bleach	Arsenite method			Photometric method		
	$[\text{OCl}^-] / 10^{-3}$ M	$s / 10^{-2}$	CV / %	$[\text{OCl}^-] / 10^{-3}$ M	$s / 10^{-2}$	CV / %
Jik	4.09	± 2.0	4.95	4.10	± 0.30	0.09
Ace	4.41	± 2.6	5.86	4.48	± 0.20	0.39
Saubermann	3.43	± 1.6	4.72	3.47	± 0.80	0.23
Shoprite	2.69	± 1.8	6.90	2.71	± 0.60	0.22

s = standard deviation and CV = coefficient of variation.

Hypochlorite determination in commercial bleaches

The four commercially available bleaches in the market were investigated, which include Jik, Ace, Saubermann and Shoprite bleach, which form part of the popular common brands used in South African households. Each bleach sample was made up to various dilutions and then analyzed, first by the arsenite method and then by the photometric method.

Example. 1.0 mL of commercial bleach (Jik) was diluted to 100 mL. 10.0 mL of the diluted sample was titrated with 0.025 M As_2O_3 according to the arsenite method. Volume of As_2O_3 consumed in triplicate runs (0.85, 0.90 and 0.80 mL; mean 0.85 mL). Thus, from the titration method,

$$[\text{OCI}^-] = \frac{(2)(0.025\text{M})(0.85\text{ mL})}{10} = 4.25 \times 10^{-3}\text{ M}, s = \pm 0.25 \times 10^{-3}\text{ and CV} = 5.88\%$$

5.0 mL of the diluted Jik sample was reacted with 5 mL of standard arsenite solution following the other identical procedures as for the calibration curves. Addition of 20.0 mL of stock permanganate showed residual pink colour. Therefore, the calibration curve 4, $y = 183.72x - 0.2977$ was used. The OCI^- determination was carried out in triplicate and the average absorbance was considered. Absorbance values in triplicate runs were (0.4618, 0.4610 and 0.4605; mean 0.4611) and $[\text{OCI}^-] = 4.13 \times 10^{-3}\text{ M}$, $s = \pm 0.01 \times 10^{-4}$ and $\text{CV} = 0.0\%$. Similarly the concentration of hypochlorite in four chosen commercial bleaching agents were determined and compared with the arsenite method results. The results of triplicate runs together with standard deviation and coefficient variation are summarised in Table 4.

Table 4. Comparison of results: arsenite *versus* photometric methods.

{For photometric method, volume of bleach reacted = 5.0 mL, $[\text{As}_2\text{O}_3] = 1.25 \times 10^{-3}\text{ M}$; $[\text{H}_2\text{SO}_4] = 0.50\text{ M}$; $[\text{KI}] = 1.0 \times 10^{-7}\text{ M}$ and $\text{KMnO}_4 = 5\text{-}20.0\text{ mL of } 2.50 \times 10^{-3}\text{ M}$ }.}

Bleach	Arsenite method-1			Photometric method-2			F-test					
	$[\text{OCI}^-]/10^{-3}\text{M}$	$s/10^{-3}$	CV / %	$[\text{OCI}^-]/10^{-3}\text{M}$	$s/10^{-3}$	CV / %	n	Fcrit	Fcalc	P	V Method 1	V Method 2
Jik	4.00	0.17	4.17	4.10	0.08	1.86	9	3.44	4.79	0.0199	2.78×10^{-8}	5.80×10^{-9}
Jik*	3.28	0.43	13.1	3.95	0.17	4.38	9	3.44	6.21	0.0092	1.86×10^{-7}	2.99×10^{-8}
Ace	4.42	0.17	3.90	4.48	0.04	0.86	12	2.82	19.96	<0.00001	2.97×10^{-8}	1.49×10^{-9}
Ace**	4.03	0.35	8.7	4.37	0.04	0.99	9	3.44	66.64	<0.00001	1.25×10^{-7}	1.87×10^{-9}
Shoprite	2.68	0.11	4.24	2.71	0.03	0.97	11	2.98	6.72	0.0029	5.04×10^{-9}	7.51×10^{-10}
Saubermann	3.44	0.13	3.88	3.47	0.02	0.63	12	2.82	36.33	<0.00001	1.78×10^{-8}	4.90×10^{-10}

s = standard deviation; CV = $s \times 100/\text{mean } [\text{OCI}^-]$ = coefficient of variation; V = variance from f-test. *diluted with distilled water; **diluted with tap water. Null hypothesis: There is no significance difference between method1 and method2 with respect to efficiency.

To investigate the limitation of the method, tap water was used for dilution of different batches of selected commercial bleaches. No problems were encountered in the determination procedures and the analytical results agreed well with control experiments using double distilled water.

A perusal of the results in Table 3 clearly indicates that data obtained by using the arsenite (method 1) and the spectrophotometric (method 2) methods are in general concurrence. To

compare the efficiency of the two methods, f-test was conducted with the null hypothesis that two methods have no difference with respect to efficiency. The f-test results are summarized in Table 4. The F-calculated values much higher than F-critical and very low probability values clearly suggest that the hypothesis is proved wrong. Further high variance values for relative to the arsenite method relative to the photometric method confirms that method 2 is superior in terms of reproducibility and efficiency.

Thus, the proposed method will prove to be handy procedure for routine determination of the strength of bleaching agents containing hypochlorite even with large number of samples. The limitation of the photometric methods is the dependence on the clarity and transmittance of the solution. Samples either non-homogenous or turbid could result in false absorbance values leading to erroneous results. Colour additives in the bleach sample, which could absorb at 525 nm may interfere in the procedure. In such a case, blank correction need to be applied.

CONCLUSION

Results from the new method are highly reproducible and with low standard deviation and variance not only relative to the arsenite method, but also to the kinetic-analytical method involving indigocarmin-hypochlorite reaction [9]. The four bleaches analysed have different matrixes, but had no significant effect on the analytical data, which supports the scope of method for the hypochlorite determination in commercial samples. The detection range for the photometric method is from 2.5×10^{-4} to 2.35×10^{-2} M OCl^- . For high OCl^- concentrations, appropriate dilution of the sample will be adequate. Very high or low $[\text{OCl}^-]$ out side the analysis range, can also be estimated, through adjusting initial As_2O_3 and KMnO_4 concentrations appropriately.

ACKNOWLEDGEMENTS

Authors thank the University of Durban-Westville (currently University of KwaZulu-Natal) and the National Research Foundation, Pretoria for the financial support to this work. Authors also thank Dr. H.R. Puttur, Department of Statistics, UKZN for his help in the statistical analysis.

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