

Exploitation of chloride ion selective electrode for determination of some chloro-oxygenated agents with iodide in the acidic medium.

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ABSTRACT

It was confirmed in this research that Cl^- ISE was successfully used in the determination of chloro-oxygenated agents involving hypochlorite, chlorite, chlorate and perchlorate in their individual and mixture aqueous solutions. The results obtained are comparable to those obtained by Pt electrode since the reactions are oxidation-reduction reactions at which Pt electrode responds directly to potential change of these reactions. The response of Cl^- ISE was slower than the response of Pt electrode, because with Cl^- ISE the liberated Cl^- was distributed in the solution toward the electrode membrane where the potential response takes place as a result of ion exchange with chloride electrode membrane. As a result the error percentages are positive with Cl^- ISE. In case of Pt electrode it is directly responded to potential difference through potentiometric titration therefore, the response at equivalence point is clear. The potentiometric titration with both electrodes gave clear jump at equivalence point and the titration curves are in S forms. Good and encouraging results were obtained with concentrated solutions as well as with diluted solutions of these agents. While the first and second derivatives offered more accurate equivalence points. The results obtained with individuals and mixtures of the chloro-oxygenated agents were almost the same or close to each other and the variance was attributed to practical errors. Both electrodes were applied for determination of hypochlorite in commercial bleaching solution. The electrodes offered result lower than that on bottle label. These may be due to wasting of the compound by high temp., transferring and agitation of the solution.

Introduction:

Chloro-oxygenated agents are significant agents as oxidizing agents and bleaching materials (table. 1)^(1,2). Therefore, different methods were used to detect and determine them. Absorption spectroscopy in IR region was used to determine KClO_4 in Tobacco which is used to reduce combustion point of Tobacco⁽³⁾. A mixture of Cl^- , ClO_2^- and ClO_3^- was determined by titration with AgNO_3 in 70% methanol using Cl^- ISE⁽⁴⁾. The precision of the method is better than 2%. The bleaching solution of hypochlorite contains always ClO_3^- and ClO_4^- ions. Therefore, these two ions should be checked to find out whether they are present or not as contaminants^(5,6).

A method of titration by injection was presented by Pacey and others⁽⁷⁾ for determination of ClO_3^- and ClO_2^- in order to avoid O_2 interfere.

Table (1) some physical and chemical properties of chloro-oxygenated agents.

| Components | Potential V | density g/cm ³ | Melting point C° | Boiling point C° | Solubility in water g/100m(25°) |
|------------------|-------------|---------------------------|------------------|------------------|---------------------------------|
| NaClO_4 | 1.389 | 2.499 | 468 | 482 | 209.6 |
| KClO_3 | 1.451 | 2.34 | 356 | 400 | 8.61 |
| NaClO_2 | 1.157 | 2.51 | 180-200 | 296 | 39.6 |
| NaClO | 0.9 | 1.11 | 18 | 101 | 29.3 |

Duty and Ward⁽⁸⁾ published paper about determination of ClO_3^- by titration with NaNO_2 as reducing agent. The liberated Cl^- was determined gravimetrically with Ag^+ . Ion chromatography was

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used to determine Cl^- , ClO_3^- and ClO_4^- in acidic solution with linear range of 1-50 mg/L and detection limit of 0.3 mg/ml⁽⁹⁾. Pirogove and others⁽¹⁰⁾ have determined ClO_3^- and ClO_4^- by using electrical migration techniques after addition of propanol to the carrier medium. Because of high stability and high resisting to reduction, perchlorate was used as supporting electrolyte in large range of potential in voltametric methods⁽¹¹⁾. An ion selective electrode was fabricated for determination of perchlorate in aqueous solution⁽¹²⁾. The linear range and slope of electrode response were $1-10^{-6}\text{M}$ and 60.6 ± 1.0 mV/decade respectively. It is applied successfully in the determination of perchlorate in urine and water. Spectrophotometric method was applied to determine ClO_3^- in drinking water in the presence of ClO_2^- . The method was simple, rapid and accurate and in comparison with ion chromatographic method⁽¹³⁾. Rosa and others used Cl^- ISE periodically⁽¹⁴⁾ to follow the concentration of added Cl^- to the pool water and to control its concn in the range of 0.2-5 ppm. Bartel and others determined Cl^- in the presence of I^- as interferent using Cl^- ISE⁽¹⁵⁾.

The electrode offers Nernstion slope 56.3 ± 0.6 mV/decade and detection limit less than 10^{-4} and selectivity factor of K_{Cl^-} , I^- Pot = 5×10^{-3} . Cl^- ISE was used to determine Cl^- in cement⁽¹⁶⁾, in pharmaceutical materials⁽¹⁷⁾, in drinking water⁽¹⁸⁾ and tap water of karck region in Baghdad⁽¹⁹⁾. Many attempts were performed to manufacture of ISES to determine ClO_4^- . A solid electrode based on copper complex with ligand doped with PVC for ClO_4^- determination in the range of 10^{-6} - 10^{-1}M with slope of 59.4 ± 0.3 mV/decade and detection limit of $4 \times 10^{-4}\text{M}$ ⁽²⁰⁾. Stanford and others^(21,22) have presented a paper insured the presence of ClO_4^- , ClO_3^- and BrO_3^- in the manufacture of hypochlorite. The investigators concluded that the suitable manufacture of hypochlorite, good storing circumstances and good careful treatment with hypochlorite will decrease the ClO_4^- , ClO_3^- and BrO_3^- formation. Anoop Ray and Murnga have devoted a detailed study⁽²³⁾ about the contamination by ClO_4^- . They investigated prafered procedure aimed to remade ClO_4^- and the effect of environmental factor on the microbic wasting of ClO_4^- .

This paper mentioned methods of remove ClO_4^- from water and the effects of temp, pH, salinity dissolved oxygen, NO_3^- , NO_2^- , Mo, SO_4^{2-} and iron on the microbic spoiling of ClO_4^- determination. It is

concluded from the above review that most of the methods included individual or two components in their solution. However, all chloro- oxygenates react with iodide and the common product is Cl^- ions. Therefore, chloride ion selective electrode was attempted to determine these oxidizing agents in their individuals and mixtures in the acidic solution compared with Pt electrode, which responds to potential variation of oxidation-reduction titration of these compounds, which are the objective of this paper.

Experimental:

Chemicals:

All chemicals used in this research are either highly graded or ANALAR purchased from BDH and Fluka companies and used without pretreatment. All solutions prepared in this research were supplied in twice distilled water at 25C° . and used Cl^- ISE, Pt electrode and Double junction Calomel electrode all electrodes from METTLER-TOLEDO (China) company.

Standardization of KI solution:⁽²⁴⁾

10 ml of KI solution were transferred into conical flask and titrated with an excess of 0.1 N AgNO_3 solution from burette, 3-4 drops of Fe^{3+} solution were added in addition to 6M HNO_3 and back titrated with 0.1N SCN^- solution till the appearance of red solution. The titration was repeated several three times and the near value of the KI solution was found.

Starch solution:

1.0 g of soluble starch was treated with small volume of water to prepare its paste which mixed well and poured in 100 ml of boiled distilled water and boiled for 1 min and left to cool and kept in firmly closed bottle.

Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ solution with KIO_3 standard solution:

10 ml of 0.1 N of KIO_3 solution was transferred into conical flask and 10 ml of 10% KI solution was added with 5 ml of 2 N H_2SO_4 . The liberated I_2 was titrated with $\text{Na}_2\text{S}_2\text{O}_3$ solution until the light yellow, 1-2 ml of starch solution was added, titration was resumed until colorless. The titration was repeated three times and the concentration was found 0.0943 N.

Standardization of iodine solution with As_2O_3 :

2.5 g of As_2O_3 was transferred into beaker and dissolved in 40 ml of 2M NaOH and neutralized with 2M H_2SO_4 until acidic. The whole solution was transferred into 500 ml volumetric flask and solution was completed to the mark with distilled water. 10 ml of this solution was transferred into conical flask, 1 g of NaHCO_3 was added with agitation and titrated with I_2 solution from burette until permanent blue colour was obtained after addition 1 ml of starch solution. The titration was repeated three times and the concentration of I_2 solution was found 0.0918 N.

Standardization of I_2 solution with standardized solution of $\text{Na}_2\text{S}_2\text{O}_3$:⁽²⁴⁾

10 ml of I_2 solution was transferred into conical flask and titrated with $\text{Na}_2\text{S}_2\text{O}_3$ solution until the solution became light yellow, 1 ml of starch solution was added and titration was resumed until colorless. The titration was repeated three times and concn of. I_2 solution was calculated to be 0.0931N.

Standardization of Na_2SO_3 solution :⁽²⁵⁾

25ml of Na_2SO_3 solution was transferred into conical flask and 23ml of I_2 solution was added and 5ml of 2N HCl. The excess of I_2 solution was titrated with standardized solution of $\text{Na}_2\text{S}_2\text{O}_3$ until colourless and the concentration of Na_2SO_3 was calculated to be 0.0902N.

Standardization of chloro-oxygenated: NaClO , $5\text{H}_2\text{O}$, NaClO_2 , KClO_3 and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$:

Approximately 0.1 N of each salt solution in twice distilled water was prepared and diluted with 30 ml distilled water and excess of standardized solution of I_2 (5 ml of 0.1% OsO_4 solution to both chlorate and perchlorate solution as activators) and 30 ml of 9 N H_2SO_4 were added. The solution was titrated with either $\text{Na}_2\text{S}_2\text{O}_3$ or Na_2SO_4 standardized solution until light yellow colour. 1ml of starch solution was added and the titration was resumed until colourless. The concentrations were found to be 0.0778N $\text{NaClO} \cdot 5\text{H}_2\text{O}$, 0.0907N NaClO_2 , 0.0982N KClO_3 and 0.1288N $\text{NaClO}_4 \cdot \text{H}_2\text{O}$.

Determination of chloro-oxygenated agents in their 0.001-0.1N concentration using Cl^- ISE and Pt electrode:

10ml of each chloro-oxygenated agent was transferred to the titration flask, 30ml of distilled water

was added in addition to 30ml of 9M H_2SO_4 (5ml of OsO_4 0.1% was added to ClO_3^- and ClO_4^- solution as activators). Both Cl^- ISE and Pt electrode and calomel ref. electrode were immersed in the solution and titrated with standardized iodide solution with stirring by magnetic stirrer until sudden change in potential. The titration was continued for several additions after equivalence point to get complete potential titration curve.

Standardization of double junction glass electrode:

This electrode was standardized with pH_4 standard solution and pH_9 standard solution in order to follow the pH change through titrations and find out its response efficiency.

Calibration of Cl^- ISE:

The Cl^- ISE was calibrated with standardized solution of Cl^- in the range 10^{-5} - 10^{-1} M with stirring by magnetic stirrer. The calibration was done in aqueous solution of Cl^- and in 0.1N KNO_3 solution. The calibration was repeated several times, the slope was found for each calibration, and the mean was calculated.

Potential selectivity caffeine measurements^(26, 27): $K_{\text{Cl}^-, \text{I}^-}^{\text{Pot}}$

Mixed solution method was applied to find out the effect of added I^- solution on the response of Cl^- ISE. The concentration of I^- was kept constant and a series of Cl^- solution was added (10^{-5} - 10^{-1}) M. The method was performed with iodide concentrations of 10^{-3} , 10^{-4} and 10^{-5} respectively. The potential was plotted against $\log [\text{Cl}^-]$ and $K_{\text{Cl}^-, \text{I}^-}^{\text{Pot}}$ was calculated.

Determination of bleaching commercial solution:

10g of commercial bleaching solution of hypochlorite was accurately weighed and transferred to volumetric flask (250ml) and completed to the mark with distilled water. 10ml of this solution was transferred into conical flask and diluted with distilled water. Accurate volume of iodide solution was added and the whole solution was titrated with thiosulphide solution using starch as indicator. The titration was repeated several times and the mean was calculated and used to find out the percentage of hypochlorite in this commercial bleaching solution. The method was repeated by transferring 10ml of bleaching solution to a beaker, diluted with 30ml of distilled water and 30ml

of 9M H₂SO₄. The solution was titrated with standardized iodide solution using Cl⁻ ISE and Pt electrode with calomel ref. electrode until complete S curves are obtained and the percentage of ClO⁻ was calculated and compared with the above manual procedure.

Determination of chloro-oxygenated agents in their mixture:

Two, three and four components of chloro-oxygenated agents were determined in their mixture using Cl⁻ ISE and Pt electrode with calomel reference electrode. A typical titration curves were obtained and the component concentration curves were compared with their individual component concentration curves in addition to their error percentages.

Results and discussion:

Calibration of Cl⁻ ISE:

The Cl⁻ ISE gave linear response range for 10⁻⁵-10⁻¹M of Cl⁻ solution, with slope of -53.8 ± 0.68 mV/decade and $R^2 = 0.9997$. The response was good and response time is less the 7 seconds (Fig. 1. a). Fig. 1. b shows the calibration of the electrode for 10⁻⁵-10⁻¹M in 0.1 N KNO₃. The response was more efficient with slope of -55.4 ± 0.73 mV/decade and $R^2 = 0.9984$. The electrode response is rapid (less than 3 sec) more stable than the aqueous solution (Fig. 1. b).

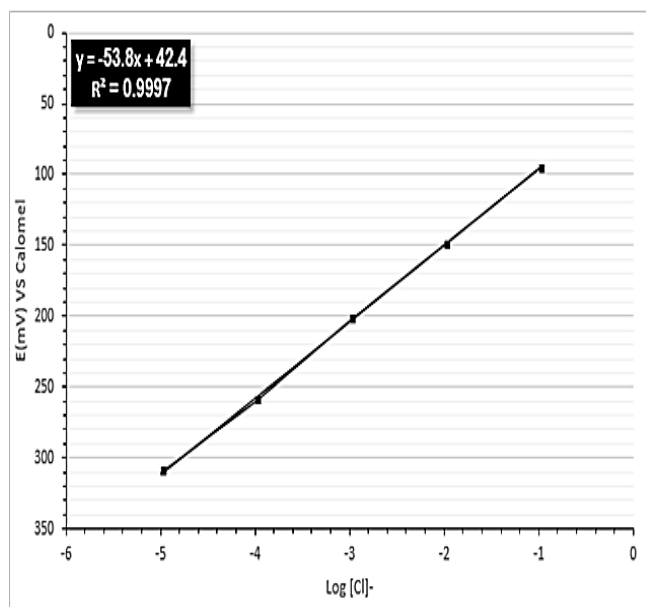


Fig. 1. a

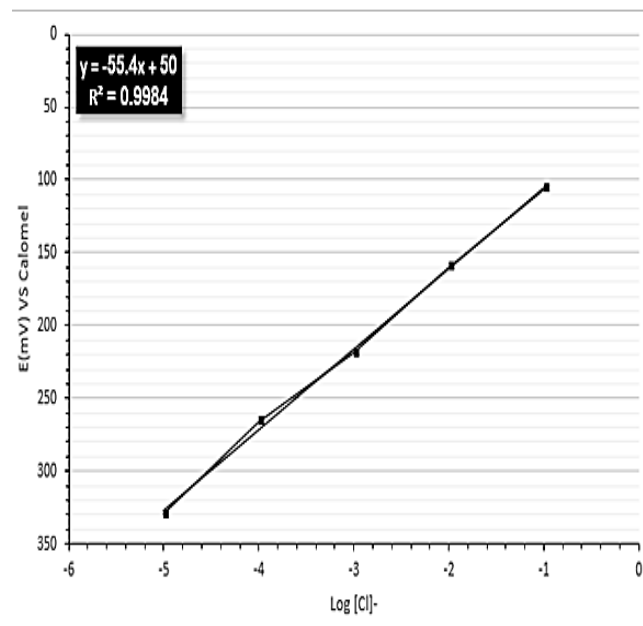
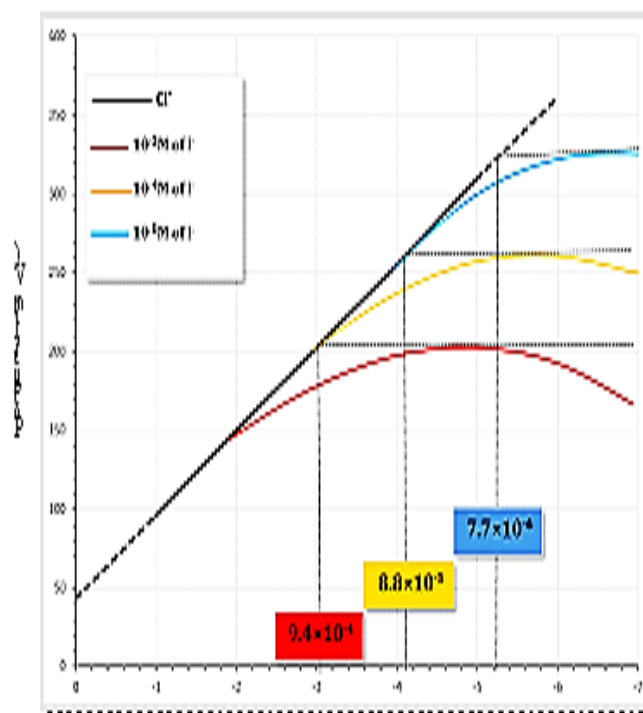


Fig. 1. b

Potential selectivity factor of Cl⁻ ISE:

Mixture solution method was applied to calculate the potential selectivity factor of Cl⁻ ISE toward Cl⁻ in the presence of I⁻ (Fig. 2).

The method showed interferences in the range of 0.77- 0.94 (Table. 2). Although these are, low but they are positive which indicate to some extents the interference of I⁻ ions.



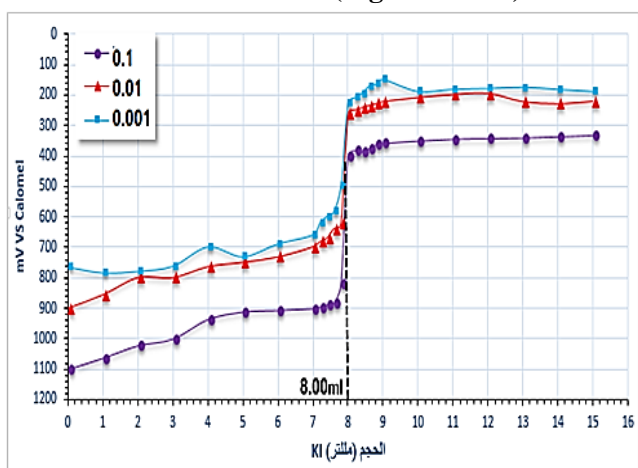
(Fig 2): Titrations curves of Cl⁻ ISE toward Cl⁻ in the presence of I⁻

Table (3): Results of the Potential selectivity factor of Cl^- ISE

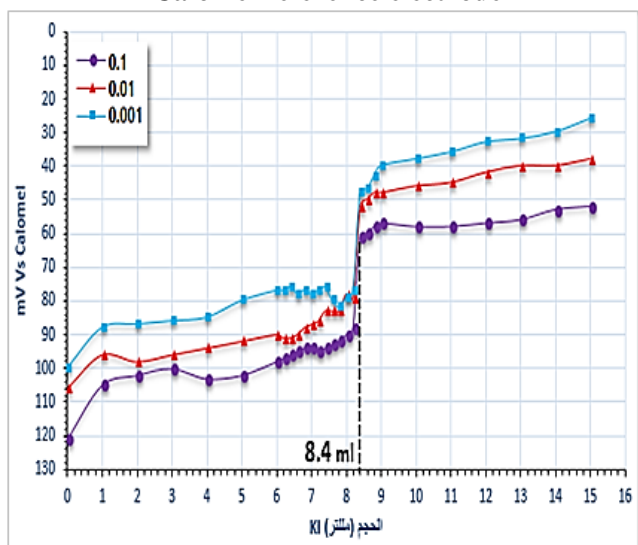
| Concentration of I^- | K^{Pot} |
|-------------------------------|------------------------|
| 10^{-3} | 7.72×10^{-1} |
| 10^{-4} | 8.812×10^{-1} |
| 10^{-5} | 9.406×10^{-1} |

Potential titration curves of chloro-oxygenated agents in concentration range of 10^{-3} - 10^{-1} M: using Cl^- ISE and Pt electrode against calomel ref. electrode.

Fig 3a and b showed the titrations curves of hypochlorite with iodide in acidic solution with different concentrations. The titration showed clear sudden changes at equivalence points and S form of the curve (Fig. 3a. and b), which were supported by first and second derivatives (Fig. 4a. and b).

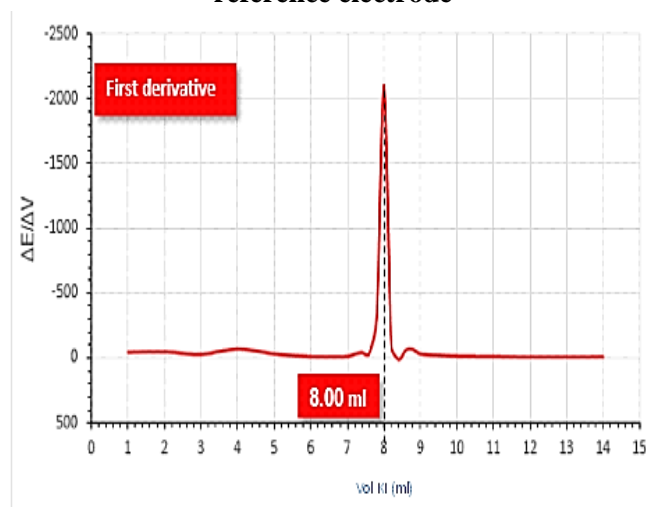


(Fig 3.a): Titrations curves of hypochlorite with iodide in acidic solution with different concentrations by using Pt electrode versus Calomel reference electrode

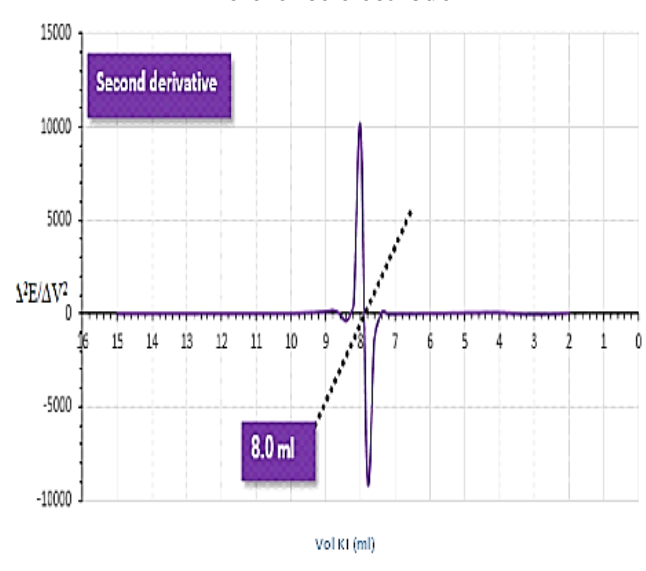


(Fig 3.b): Titrations curves of hypochlorite with iodide in acidic solution with different concentrations by using Cl^- ISE versus Calomel reference electrode

concentrations by using Cl^- ISE versus Calomel reference electrode



(Fig 4.a) First derivative to titration curve of the sodium hypochlorite solution with standardized iodide solution using Cl^- ISE versus Calomel reference electrode



(Fig 4.b) Second derivative of titration curve of the sodium hypochlorite solution with standardized iodide solution using Cl^- ISE versus Calomel reference electrode.

In order to find out the efficiency of both electrodes toward the chloro-oxygenated agents the added quantity and its recovery were calculated in addition to errors percentages. Table (3) shows titration results of these compounds with iodide solution in acidic media.

Table (3): Potential titration results of chloro-oxygenated agents with iodide in acidic solution with different concentrations.

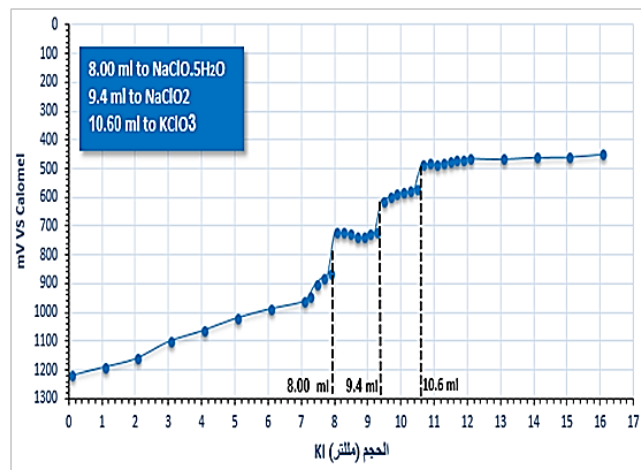
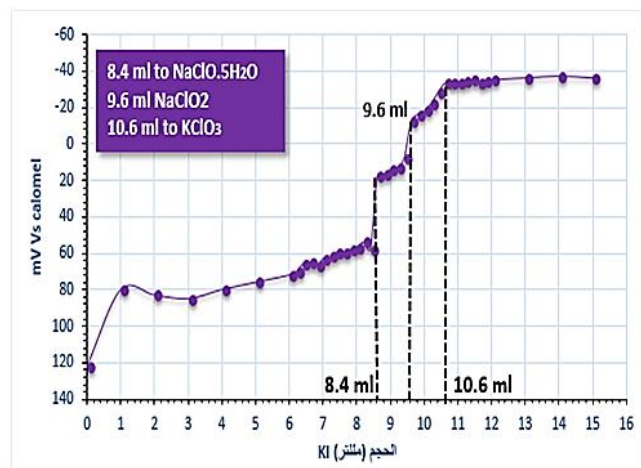
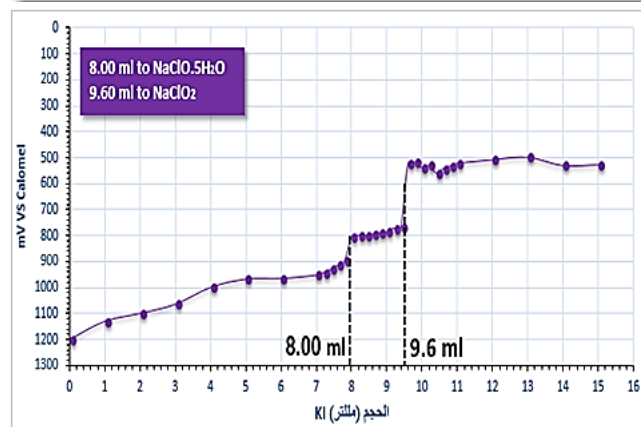
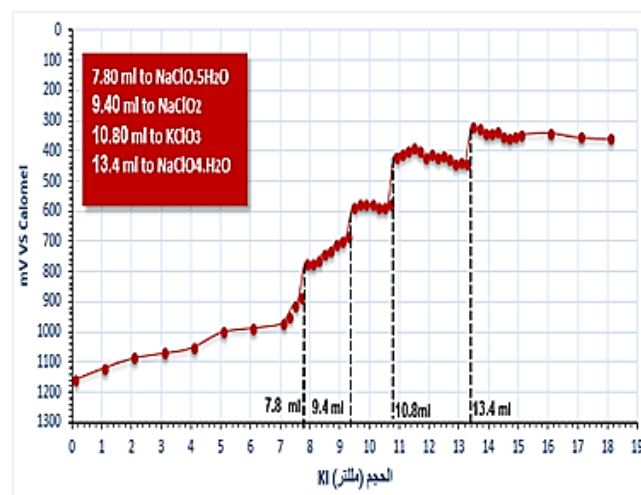
| No. | Components | The Electrode | Added quantity (ppm) | Recovery (ppm) | Error Percentage % |
|-----|---------------------------------------|-----------------|----------------------|----------------|--------------------|
| 1. | NaClO ₂ .5H ₂ O | Pt | 6394 | 6193 | -3.1 |
| | | | 639 | 619 | -3.1 |
| | | | 63 | 62 | -3.1 |
| | | Cl ⁻ | 6394 | 6500 | +1.6 |
| | | | 639.4 | 650 | +1.6 |
| 2. | NaClO ₂ | Pt | 2050 | 1959 | -4.4 |
| | | | 205 | 200 | -2.4 |
| | | | 20.5 | 20.4 | -0.4 |
| | | Cl ⁻ | 2050 | 2044 | -0.3 |
| | | | 205 | 204.4 | -0.3 |
| 3. | KClO ₃ | Pt | 2005 | 2000 | -0.24 |
| | | | 200.5 | 200 | -0.25 |
| | | | 20.05 | 20 | -0.25 |
| | | Cl ⁻ | 2005 | 2077 | +3.6 |
| | | | 2005 | 207.7 | +3.5 |
| 4. | NaClO ₄ .H ₂ O | Pt | 2260 | 2314 | +2.3 |
| | | | 226 | 231.4 | +2.3 |
| | | | 22.6 | 22.8 | +0.88 |
| | | Cl ⁻ | 2260 | 2350 | +3.9 |
| | | | 226 | 238.0 | +5.3 |
| | | | 22.6 | 24.1 | +6.6 |

Looking through table 3, it was concluded that the error percentages were from -4.4% to +6.6% which were attributed to practiced errors in addition to iodide interferences in Cl⁻ ISE responses which gave positive errors.

The results also clarified the high efficiency of both electrodes for determination of chloro-oxygenated agents in their individual acidic solution.

Potential titration results for mixtures of chloro-oxygenated agents in acidic solution:

Fig 5 shows a typical potential titration curves for two, three and four chloro-oxygenated agents in their acid solutions. The equivalence points are clear and promising in calculating the concentration of these compounds which almost in coincidence with the individuals of agents solution (table 4) and (table 5).



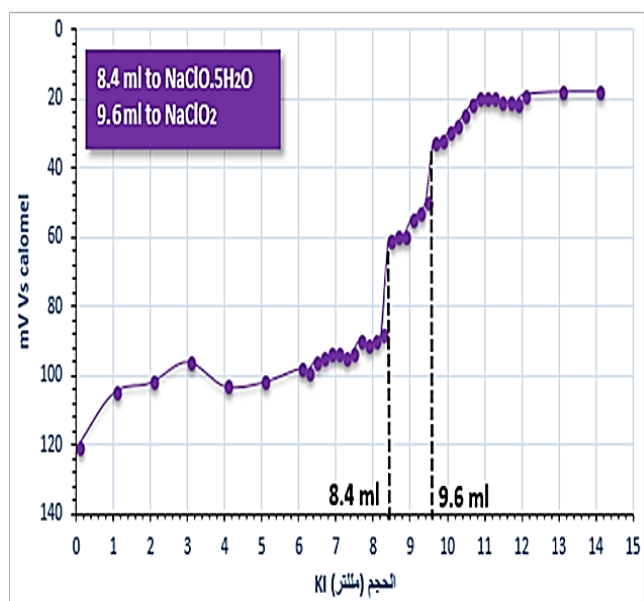


Fig (5): Typical potential titration curves for two, three and four chloro-oxygenated agents using Pt & Cl⁻ electrodes versus Calomel reference electrode.

Table (4): Potential titration results of mixtures of the chloro-oxidizing salts using Pt electrode.

| No. | The mixture | Added uantity (ppm) | Recovery (ppm) | Error Percentage % |
|-----|---|------------------------------|------------------------------|------------------------------|
| ١ | NaClO.5H ₂ O + NaClO ₂ | 6394 2050 | ٦١٩٣ ٢٠٤٤ | -3.1 -0.26 |
| ٢ | NaClO.5H ₂ O + KClO ₃ | 6394 ٢٠٠٥ | ٦١٩٣ ٢٠٣٩ | -3.1 +1.6 |
| ٣ | NaClO.5H ₂ O + NaClO ₄ .H ₂ O | 6394 2260 | ٦١٩٣ ٢٢٨٠ | -3.1 +0.88 |
| ٤ | NaClO ₂ + KClO ₃ | 2050 ٢٠٠٥ | ٢٠٠٢ ٢٠٣٩ | -2.3 +1.6 |
| ٥ | NaClO ₂ + NaClO ₄ .H ₂ O | 2050 2260 | ٢٠٠٢ 2280 | -2.3 +0.88 |
| ٦ | KClO ₃ + NaClO ₄ .H ₂ O | ٢٠٠٥ 2260 | ٢٠٣٩ ٢٢٨٠ | +1.6 +0.88 |
| ٧ | NaClO.5H ₂ O + NaClO ₂ + KClO ₃ | 6394 2050 ٢٠٠٥ | ٦١٩٣ 2002 ٢٠٣٩ | -3.1 -2.3 +1.6 |
| ٨ | NaClO.5H ₂ O + NaClO ₂ + NaClO ₄ .H ₂ O | 6394 ٢٠٥٠ 2260 | ٦١٩٣ ٢٠٠٢ ٢٢٨٠ | -3.1 -2.3 +0.88 |
| ٩ | NaClO.5H ₂ O + KClO ₃ + NaClO ₄ .H ₂ O | 6394 ٢٠٠٥ 2260 | ٦١٩٣ ٢٠٣٩ ٢٢٨٠ | -3.1 +1.6 +0.88 |
| ١٠ | NaClO ₂ + KClO ₃ + NaClO ₄ .H ₂ O | 2050 ٢٠٠٥ 2260 | ٢٠٠٢ ٢٠٣٩ ٢٢٨٠ | -2.3 +1.6 +0.88 |
| ١١ | NaClO.5H ₂ O + NaClO ₂ + KClO ₃ + NaClO ₄ .H ₂ O | 6394 2050 ٢٠٠٥ 2260 | 6038 2002 2077 ٢٢١٥ | -5.7 -2.3 +3.6 -1.9 |

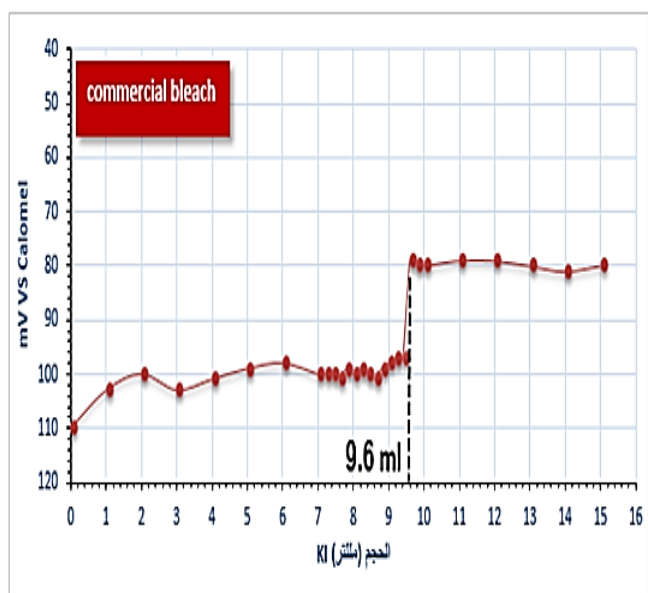
Table (5): Potential titration results of mixtures of the chloro-oxidizing salts using Cl⁻ ISE.

| No. | The mixture | Added quantity (ppm) | Recovery (ppm) | Error Percentage % |
|-----|--|----------------------|----------------------|----------------------|
| ١ | NaClO.5H ₂ O + NaClO ₂ | 6394 2050 | ٦٠٠٣ ٢٠٤٤ | +1.7 -0.3 |
| ٢ | NaClO.5H ₂ O + KClO ₃ | 6394 ٢٠٠٥ | ٦٠٠٣ ٢٠٣٩ | +1.7 +1.7 |
| ٣ | NaClO ₂ + KClO ₃ | 2050 ٢٠٠٥ | ٢٠٤٤ ٢٠٣٩ | -0.3 +1.7 |
| ٤ | NaClO.5H ₂ O + NaClO ₂ + KClO ₃ | 6394 2050 ٢٠٠٥ | ٦٠٠٣ ٢٠٤٤ ٢٠٣٩ | +1.7 -0.3 +1.7 |

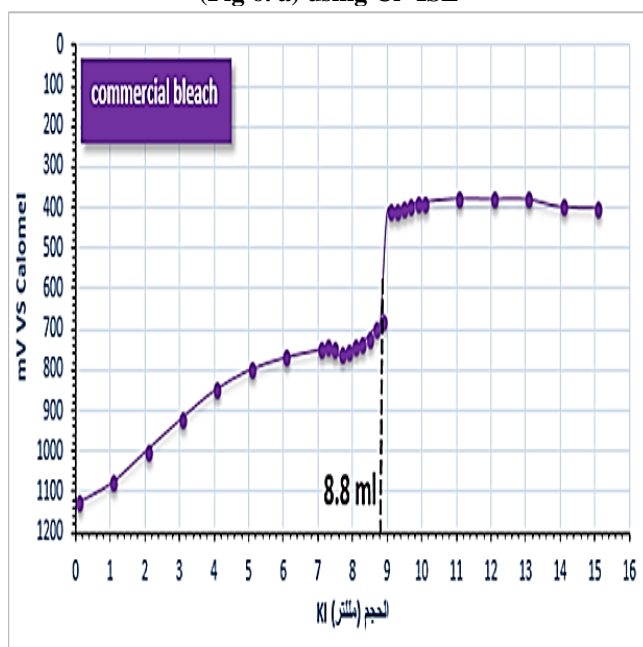
NaClO₄.H₂O was not included in the determination of mixtures by Cl⁻ ISE because of its difficulty in reducing and the equivalence point was not so clear in the mixture. However, its equivalence point was clear in its individual solution since 0.1% of OsO₄ was added as activator.

Determination of hypochlorite in commercial bleaching solution:

Hypochlorite was determined in commercial bleaching solution (Iranian sample) (not more than 5%) by titration with standardized iodide solution using Cl⁻ ISE and Pt electrode. (Fig 6 a and b). The liberated iodine was titrated with standardized thiosulphate solution for comparison (table 6).



(Fig 6. a) using Cl^- ISE



(Fig 6. b) using Pt electrode

Table (6) shows the potential titration results with manual titration results for comparison.

| Component | The electrode | Evaluated result by using normal titration method with thiosulphate solution | Evaluated result by using potentiometric titration method with iodide solution | Percentage error % |
|-----------|-----------------|--|--|--------------------|
| NaClO | Cl ⁻ | 3.24% | 3.37% | +4.0 |
| | Pt | 3.24% | 3.10% | -4.3 |

The percentage of hypochlorite results in potential titration methods relative are less than the value on the bottle label (5%). The error percentage are

+4.0% with Cl^- ISE and -4.3% with platinum electrode. The lower values obtained with both electrodes and even with manual titrations were due to the wasting of the compound during long storing, the effect of high temp, and during transferring, dilution and stirring^(28,29).

Conclusions:

1. It is confirmed in this research the efficiency of Cl^- ISE and Pt electrode in determination of chloro-oxidizing agent in iodimetric titration in acidic solution.
2. It is possible to determine these compounds individually and in their mixtures using Cl^- ISE and Pt electrode.
3. The possibility of application of Cl^- ISE and Pt electrode in determination of hypochlorite in commercial bleaching solution.

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References:

1. Cotton, F. Albert. and Wilkinson, Geoffrey (1988), Advanced Inorganic Chemistry (5th ed.), New York: Wiley-Interscience, p. 564.
2. Sellers, K., Alsop, W., Clough, S., Hoyt, M., Pugh, B., Robb, J. and Weeks, K. (2006). CRC Press: Boca Raton, FL, USA, P 177.
3. Tong, Tsumg – Folond Gordon, Gilbes, (1980). Anal. Chem. (52), Pp1430 -1433.
4. Briggs, A. G., Aoyes, W .P. Howling, P. A. and Burns, D. T. (1970) Mikro Chimica Acta, Pp .888-891.
5. Aleta, R. and Hernande, Z. (1984) Jamma, 76(1), 64.
6. Ikeda, Y., Tang, T. F. and Gordon, G., (1984) Iodometric Method for Determination of Trace Chlorate Ion, Analytical Chemistry, 56(1), Pp 71-73.

7. Pacey, G., Hallowell, D. A., Miller, K. G., Straka, M. R. and Gordon, G., (1986). Selectivity Enhancement by Flow Injection Analysis, *Analytica Chimica Acta*, 178, Pp 259-267.
8. Duty, R. C. and Ward, J. S., (1994), *Analyst*, 119, Pp 2141-2143
9. Stnti, R. (1993) *Chromtographia*, 37, (5/6) Pp 300-303.
10. Pirogove, A. V., Yur'Ev, A. V. and Shpigum, O. A. (2003). *Journal of Analytical Chemistry*, 58(8), Pp 781-784.
11. Long, G. G. And Horany , G . (2003) *J .Of Electroanalytical Chemistry*, 552, Pp 197-211.
12. Ardakani, M. M., Jalger, M., Naeimi, H., Zare, H. R. and Maradi, L. (2005), *Anal Bioanal. Chem*, 381, Pp 1186-1192.
13. Hossein, S. G., Pourmortazari, S. M, And Ghalivand, Kh. (2009) *Desalination*, (Science Direct), 245, Pp 298-305.
14. Rosa, O. M., Hilin, A. N. and Graham E. N. (2009). *Flow Injection Analysis System Based On Amperometric Thin-Film Transducers Free Chlorine Detection In Swimming Pool Waters*, *Talanta*, 77, Pp 1739–1744.
15. Bartel, N, J., (2009) ” Potentiometric Determination of Iodide and Chloride in a Sample“ *J. Analy. Chem*, 213, Pp 196-203.
16. Alvarez-Romera, G., Ramirez – Silver, M, Gelan – Vidal, C. and Paez –Hernandez, M. (2010) *Electroanalysis*, 22(14), 1650-1654.
17. Khodier, I. A. H., Abdul-Wahid, M. M. and Mohammed, M. Kh. (2011) *J. Of Mustanseryah Science*, Vol. 22 (4) Pp 159-167.
18. Bratovic, A. and Odobasic, A. (2011), *Determination of Fluoride and Chloride Contents in Drinking Water by Ion Selective Electrode*, *J. Tuzla Univ .Environment Monitoring*, 6(2), Pp 109-120.
19. Nada, K. B, Hussain, Y and Mohammed, A. A. (2013), *J. Al Anbar Univ. For Pure Sciences*, 7(2), Pp 176-180.
20. Gholamian, F, Sheikh – Mohsen, M. A. Niasari, M. S. (2011). *Materials and Engineering C*, 31, Pp 1688-1691.
21. Stanford, B. D., Pisarenko, A. N., Sydeo S. A. And Gordon A. G (2011) *American Water Works Association* , 103(6), Pp 1-12
22. *Ibid*, P 71-83.
23. Anoop – Raj, J. R. and Murnga Nan Dem (2012) *J. Of Chemical, Biological and Physical Science*, Vol 2(3), Pp 1567-1584
24. *Vogels' Textbook of Quantitative Chemical Analysis*, (1998), Revised by G. H. Geffrey, T. Basset, Mendham and R.C. Denney, 12th edition, Longmans , England.
25. Williams, W. J, *Handbook of Anion Determination*. (1997). Butterworths and Co (Publishers) Ltd., P 500.
26. Al-Hitti, I. K. (2004), *Electrical Instrumental Analysis and Separation Method (1sted)*, Collage of Science. Sanaa Univ. Pp 60-62.
27. Kalsu, T., Tsunamoto, Y., Hanioka, N., Komagoe, K., Masuda, K. and Marimatsu, S. (2008). *Caffeine-Sensitive Membrane Electrode*. *Anal. Chemica. Acta.*, 620(1), Pp 50-54.
28. Lister, M. W. "Decomposition of Sodium Hypochlorite: The Uncatalyzed Reaction", (1956) *Can. J. Chem*, 34, Pp 465-478.
29. Gordon, G. and Adam, L.C. (1999) 'Hypochlorite Ion Decomposition: Effect of Temperature, Ionic Strength, and Chloride Ion' *Inorganic. Chem*, 38 Pp 1299-1304.

استثمار قطب الكلوريد الانتقائي في تقدير بعض مركبات الكلور المؤكسدة لليوديد في الوسط الحامضي.

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الخلاصة: -

أثبت هذا البحث كفاءة قطب الكلوريد الانتقائي في تقدير مركبات كلور الاوكسجينية المتضمنة الهايوكلوريت ClO^- والكلوريت ClO_2^- والكلورات ClO_3^- والبركلورات ClO_4^- في محاليلها المائية الحامضية منفردة وفي مزائج محاليلها. وقورنت هذه النتائج وعززت باستعمال قطب البلاتين لأن التفاعلات الحاصلة هي تفاعلات تأكسد واختزال حيث يستجيب قطب البلاتين للتغير في جهد اختزال مركب الكلور الاوكسجيني. لقد كانت استجابة قطب الكلوريد أبطأ من استجابة قطب البلاتين لأنه باستعمال قطب الكلوريد يتحرر الكلوريد وينتشر في المحلول حتى يصل غشاء القطب ليستجيب له نتيجة التبادل الايوني مع كلوريد القطب في الوقت الذي يحصل مع قطب البلاتين الاستجابة المباشرة للتغير بالجهد فتكون الاستجابة والتغير عند نقطة التكافؤ أوضح لهذا وجدنا نسبة الخطأ في هذه المركبات موجبة عند استعمال قطب الكلوريد إضافة الى تداخل اليوديد بينما كانت نسبة الخطأ مع قطب البلاتين سالبة. لقد اعطى التسحيح المجاهدي لكلا القطبين قفزة واضحة عند نقطة التكافؤ وكانت النتائج ايجابية وجيدة وكان منحنى التسحيح على شكل حرف S. كما تم الحصول على نتائج واضحة وجيدة عند استخدام محاليل مخففة لهذه المركبات الكلورية المؤكسدة. ولقد أعطت طريقة رسم المشتقة الأولى والثانية مقابل حجم المحلول المضاد نقاط تكافؤ ادق وأوضح. وتكاد تكون النتائج التي حصل عليها لهذه المركبات في مزائج محاليلها مساوية او مقاربة للتي تم الحصول عليها في محاليلها المنفردة بما يعزز كفاءة القطبين في تقدير هذه المركبات وعزي الاختلاف البسيط الى الخطأ التجريبي. وتم استعمال القطبين في تقدير الهايوكلوريت في محلول القاصر التجاري وقد اظهر القطبان نتائج اقل مما هو مثبت على ورقة قنينة القاصر وقد يعزى ذلك الى تحلل المركب بدرجة الحرارة وانشاء نقله وتفككه خلال عملية الرج اثناء التسحيح.