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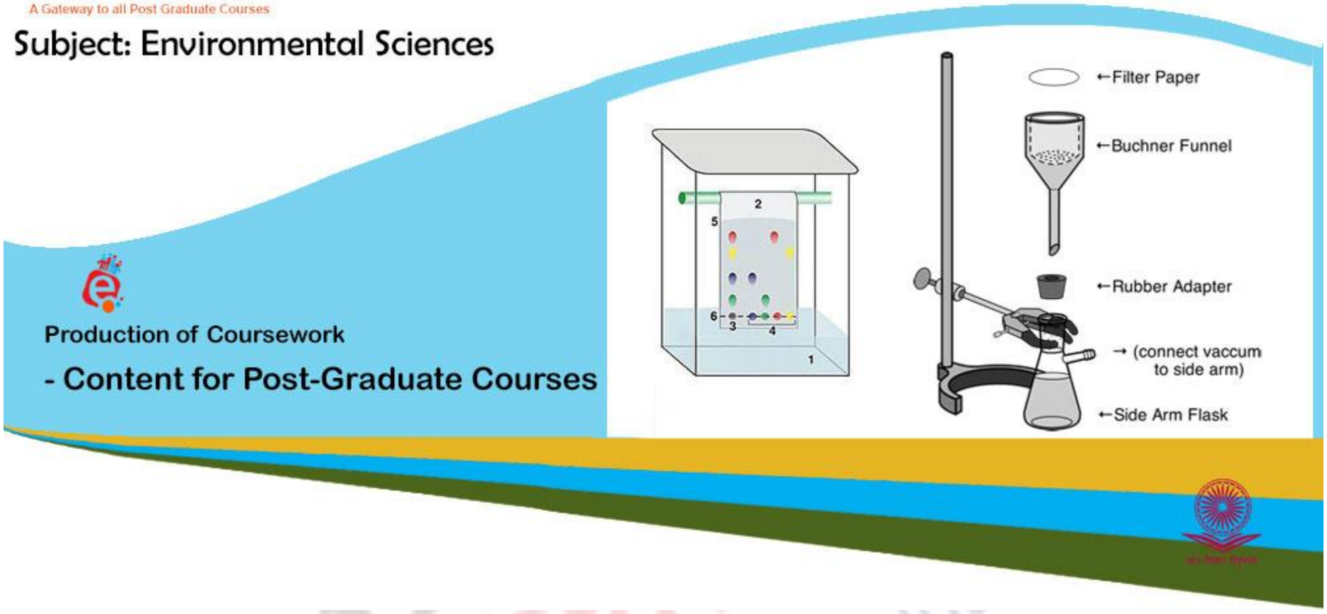

Production of Coursework

- Content for Post-Graduate Courses

Paper No: 2Analytical Chemistry

Module 6: Redox Titrations

A Gateway to all Post Graduate Courses

Development Team

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Description of Module	
Subject Name	**Environmental Sciences**
Paper Name	Analytical Chemistry
Module Name/Title	Redox Titrations
Module Id	EVS/AC-II/06
Pre-requisites	
Objectives	**To study the basics of redox titration and know the following about self generated questions.** • What is gravimetric analysis? • What are the characteristics of a good gravimetric analysis? • How does a redox indicator work? • What is cerimetry? • What is iodometry and iodimetry? • What are the applications of redox titration?
Keywords	

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1. What is gravimetric analysis?
2. What are the characteristics of a good gravimetric analysis?
3. How does a redox indicator work?
4. What is cerimetry?
5. What is iodometry and iodimetry?
6. What are the applications of redox titration?

Module 6: Redox Titrations

1. Redox titrations:

Redox titration is the titration between oxidant and reductant that may involve the use of redox indicator. Oxidation and reduction are complementary to each other and go side by side. The oxidising agent itself undergoes reduction and a reducing agent undergoes oxidation. Sometimes a reagent may act as both oxidising and reducing agent depending on the reaction condition. For example H_2O_2 can act as both oxidizing and reducing agent.

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O \quad \text{(acidic solution), 1.77 V (oxidant)}$$

$$H_2O_2 + 2e^- \longrightarrow OH^- \quad \text{(alkaline solution), 0.88 V (oxidant)}$$

Table 1: Some common oxidizing and reducing agents

Oxidising agents	Reducing agents
Permanganate	**Ferrous**
Iodine	**Thiosulphate**
Iodate	**Sulphite**
Chromate	**Hydrazine**
Hydrogen peroxide	**Stannous**
Perchloric acid	**Hydroxylamine**
Ferrate	**Borohydride**
Nitric acid	**Hypophosphorous acid**

2. Oxidising agents used in redox titration

2.1 Potassium permanganate as oxidising agent: Potassium permanganate is one of the widely used oxidising agent. It is readily available, cheap and act as self-indicator. If titrant is too dilute that its colour change is not visible, indicators like ferroin or diphenylaminesulphonic acid may be used. $KMnO_4$ needs to be standardized before titration as it is not a primary standard. The oxidising power of $KMnO_4$ depends on the medium:

Acidic medium:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + H_2O$$

In alkaline medium

$$MnO_4^- + e^- \rightarrow MnO_4^{-2}$$

In neutral or weakly alkaline medium

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + OH$$

For preparation of solution of $KMnO_4$, the weighed amount is added to distilled water and the resulting solution is heated for 15-20 min. to fasten the oxidation of any organic species that might be present in the distilled water even. The solution is filtered with the help of sintered glass crucible not with filter paper to remove MnO_2 (filter paper reacts with MnO_4 to form MnO_2). The $KMnO_4$ solution is stored in dark brown bottle to avoid sunlight. If the solution is to be used after one or two weeks it needs to be restandardize as it decomposes slowly. $KMnO_4$ should always be taken in burette with glass stopper as it attacks rubber. Being colored solution the upper meniscus is read instead of lower meniscus. Sometimes during the titration of oxalate with $KMnO_4$ the solution turns brown. It can be attributed to the fast addition of $KMnO_4$ solution or due to addition of lesser quantity of sulphuric acid added than the required amount. As $KMnO_4$ is not primary standard it needs standardization before titration. Oxalic acid, arsenic oxide, iron wires or sodium thiosulphate are used as primary standard to standardize the solution.

2.2 Potassium Dichromate as an Oxidising Agent

Dichromate ion is reduced to green chromium (III) ion in acidic medium

$$Cr_2O_7^{2-} + 14H_2O + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Potassium dichromate is not as versatile as potassium permanganate as it has lower oxidising capability and with certain reducing agents the reaction is slow. Potassium dichromate is cheap stable up to fusion point and act as primary standard. One of the major advantage of dichromate solution is that it can be used for titrimetric determinations of metal ions where solution is formed in HCl also as it does not oxidise HCl to chlorine whereas $KMnO_4$ cannot be used in HCl solution. Potassium dichromate is orange in colour and colour of complexes of Cr^{+3} ranges from green to violet. Indicators like N-phenylantharanilic acid (0.1% solution in 0.005 M NaOH), diphenylamine sulphonic acid (0.2% aqueous solution) or diphenylbenzidine sulphonic acid are employed to determine the end point. Dichromate is sufficiently pure to prepare the solution directly and the solid must be dried at 150° - 200 °C before weighing. Oxidising agents such as nitrates, perchlorates and peroxides are determined indirectly. For these analyses Fe (II) is widely used, an excess amount of Fe (II) solution is added to solution of these oxidizing agents. The un reacted Fe (II) is back titrated with dichromate solution.

2.3 Cerimetry Cerium exist in two different oxidation states i. e +3 (cerous) and +4 (ceric). Cerium in +4 oxidation state acts as powerful oxidising agent in acidic medium (generally H_2SO_4). HCl and HNO_3 solutions of Ce(IV) are not preferred for most of redox titrations. Direct titration of Ce(IV) with Fe^{+2} in dilute HCl can be carried out safely. Ferroin and some substituted phenanthrolines are used as indicators. The solution of Ce^{+4} is highly stable for prolonged period in 1 M H_2SO_4, however Ce^{+4} hydrolyses to ceric hydroxide if solution is not acidic.

2.4 Iodimetry and Iodometry

Iodine is weak oxidant and iodide is a weak reductant, the reactions for iodine-iodide couple are shown as

$$I_{2(s)} + 2e \rightarrow 2I^-$$

$$I_3^- + 2e \rightarrow 3I^-$$

$$I_{2(aq)} + I^- \rightarrow I_3^-$$

Iodine has limited applications when compared with other oxidising agents due to its weak oxidising nature. It can be titrated against strong reducing agent. However this property makes it advantageous because of its selectivity for reducing agents in presence of weaker ones. Due to less stability of I_2 solution its restandardization at regular intervals is required. Iodine is weakly soluble in water and is dissolved in presence of potassium iodide. The solution should be diluted till the last trace of iodine is dissolved. The solution must be filtered on sintered glass crucible before standardization. The iodine solution must be stored in closed vessel because of its volatile nature even in presence of iodide ion. Iodine attacks some organic reagents and thus rubber stoppers or corks should be avoided. Iodometry and iodimetry are two processes to bring about iodine titrations. Iodimetry processes are those where the standard iodine solution is used as an oxidant. Iodometry processes are those in which iodine liberated (from KI) during the reaction with the action of known weight of an oxidising agent such as $CuSO_4.5H_2O$, $KMnO_4$, $K_2Cr_2O_7$ etc. in almost neutral solution. Though starch is not a redox indicator but it can be used as indicator for iodine titrations as it gives blue color even in concentration $<10^{-5}$ M. Starch solution is prepared by making paste of 2-3 g of starch with 15 ml of water. To this paste 250 ml hot water is added slowly. Decant off the clear solution. To keep the starch solution for longer time few drops of boric acid/ salicylic acid/formamide are added to prevent bacterial growth. Now a days water soluble sodium starch glycollate is used as an indicator. The direct titration of iodine solution are with SO_3^{2-}, S^{2-}, As (III), Sb(III), Sn(II) and $[Fe(CN)_6]^{4-}$. The control pH during these titrations is essential as above pH 8 the iodine reacts with OH^- ions. The titrations with iodine should not be contained in open beakers and out in direct sunlight.

For iodometry titrations medium should be almost neutral (<8), KI solution should be kept away from direct sunlight. Iodometry titrations should be carried out at 20° -25 ° C.

3. Reducing agents used in redox titrations:

3.1 Iron (II) as Reducing Agent

Iron (II) is easily prepared from Fe (II) sulfate, iron (II) ammonium sulfate (Mohr's salt), or from the closely related iron(II) ethylenediamine sulfate. To prevent air oxidation of Fe (II) solution, the solutions are prepared in 0.5 M H_2SO_4. Such solutions are stable for no more than one day. Numerous oxidizing agents are determined by treatment of the analyte solution with a measured excess of standard iron (II) followed by immediate titration of the excess with a standard solution of potassium dichromate or cerium (IV).

3.2 Sodium Thiosulfate as Reducing Agent

Sodium thiosulphate is moderately strong reducing agents for titration with iodine solution. The thiosulfate ions react with iodine to produce tetrathionate ions. pH, the presence of microorganisms, the presence of copper (II) ions, and exposure to sunlight are some of the variables that may cause the concentration of a thiosulfate solution to change by several percent over a period. The solution must be restandardize regularly.

4. Redox indicators

Redox indicators are those chemicals which do not participate in redox reaction but their color in oxidized and reduced forms is different. When the indicator is added to the analyte, it imparts different color depending on potential of solution. Upon addition of titrant to the analyte, the color of solution changes due to change in oxidation state of indicator indicating the end point.

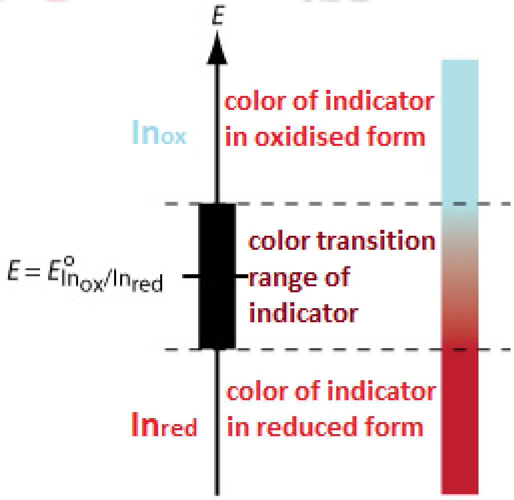


Figure 1: Redox indicators and its mechanism

5. Electrochemical Detection of End Point in Redox Titrations

The redox reaction can also be defined electrochemically, where the reaction is carried out in an electrochemical cell. In titration curve the electrochemical potential is plotted against the titrant volume. The standard electrode potential table can be helpful in determining the feasibility of reaction. Few terms related to electrochemical reactions are:

5.1 *Electric Current*: The quantity of charge flowing through a circuit in one second is current and unit of current is ampere (A).

5.2 *Electric Charge*: The magnitude of charge of single electron is 1.602×10^{-19} C. One mole of electron has charge of 9.649×10^{4} C and is known as faraday constant. The electric charge (q) is measured in terms of coulomb (C).

$$q = n \times F$$

5.3 *Free energy*: The free energy for a chemical reaction can be defined as work done by reaction on the system and unit of free energy is G. The negative sign of G shows that work is done on the surrounding.

$$\Delta G = -nFE$$

Thus $\Delta G = -qE$

6 Redox Titration Curve

Fe (II) can be determined potentiometrically with Ce (IV) titrant for which $K_{eq} = 10^{16}$ in 1 M $HClO_4$. The calomel electrode saturated with KCl solution is used as reference electrode that maintains a fixed potential. The Pt wire is used as indicator electrode that responds to analyte activity. The solution after the beginning of titration contains a mixture of Fe^{+2}, Fe^{+3}, Ce^{+3}, Ce^{+4} in the beaker. Ce^{+4} are added from burette to titrate the Fe^{+2} in beaker. The potentiometer measure the voltage driving the electrons through the meter.

The reference half reaction at calomel electrode is

$$2Hg(l) + 2Cl^{-} \rightleftharpoons Hg_2Cl_2(s) + 2e^{-}$$

At the indicator electrode, the two reactions are:

$$Fe^{+3} + e^- \rightleftharpoons Fe^{+2} \qquad E^0 = 0.767\ V$$

$$Ce^{+4} + e^- \rightleftharpoons Ce^{+3} \qquad E^0 = 1.70\ V$$

The titration curve shows three regions

Pre equivalence region: As the titration begins with the addition of Ce^{+4}, the Ce^{+4} ions are consumed and Ce^{+3} are produced. At this point concentration of Fe^{+3}, Fe^{+2} can be determined easily

Eequivalence point: Virtually all the analyte has been consumed and

$[Fe^{+3}] = [Ce^{+3}]$

Post equivalence region: There will be excess of Ce^{+4}

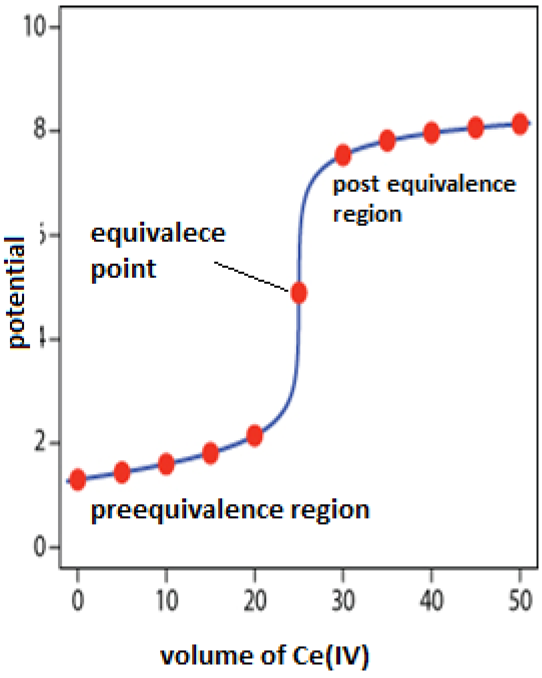


Figure 2: The potentiometric response of Fe^{+2} v/s Ce^{+4} titration

7. Applications of Redox Titrations

7.1 Determination of chromium in water Cr (III) and Cr (VI) are present in water. Cr (III) is non toxic and essential element whereas Cr(VI) is carcinogenic. Various methods are available to determine the concentration of Cr ions. One among these methods is the oxidation of the reagent 1, 5-diphenylcarbohydrazide (diphenylcarbazide) by Cr (VI) in acid solution. The reaction produces a red-purple chelate of Cr (III) and diphenylcarbazide to be monitored colorimetrically. The direct reaction of Cr (III) itself and the reagent is so slow that essentially only the Cr (VI) is measured. The sample is first titrated with permanganate to convert all the Cr (III) to Cr (VI). The excess oxidant is destroyed with sodium azide. A new colorimetric measurement is made that determines total chromium (the original Cr (VI) plus that formed by oxidation of Cr (III)). The amount of Cr (III) present is then obtained by subtracting the amount of Cr (VI) obtained in the original measurement from the amount of total chromium obtained after permanganate oxidation. Note that in this titration permanganate is being used as an auxiliary oxidizing agent.

7.2 Chemical Oxygen Demand (COD): The COD is an analytical parameter to assess the quality of waste water, drinking water and surface water. It measures the oxidizable components in water. COD is the quantity of oxygen required to convert the organic material present in water into water and carbon dioxide. The lesser is the COD value higher is the purity of water. It is not necessary that COD value may correlate with the BOD value as COD value does not differentiate stable organic matter from unstable organic matter. The COD values are determined by subtracting the oxygen consumed in given sample with the blank titration.

Principle: COD is based on the principle of back titrations where the sample is refluxed with known amount of potassium dichromate and sulphuric acid that oxidizes the organic matter present in sample producing carbon dioxide and water. The excess of potassium dichromate is titrated against Mohr’s salt using ferroin indicator.

Various interferents include chlorides, nitrites, straight chain aliphatic compounds, iron, aromatic hydrocarbon fatty acids. The addition of mercuric sulphate removes the interfering chlorides as mercuric chloride and sulphamic acid is used to remove nitrite from sample prior to addition of other reagents. The concentration of sulphuric acid is maintained at 18 N.

Procedure:

For COD sample (≥50 mg/L): Dilute the 20 ml sample solution with 20 ml distilled water. To this add 0.4 g $HgSO_4$ to remove the interference of chlorides. To this solution add 10 ml 0.25 N $K_2Cr_2O_7$ solution followed by slow addition of 30 ml of concentrated sulphuric acid. Reflux the solution for two hours. After refluxing cool the solution and titrate it against standard Mohr salt using ferroin indicator. At the end point the green color of solution changes to wine red. Reflux the reagent blank with sample under identical conditions.

The procedure for determination of COD (≤ 50 mg/L) will remain same except the normality of potassium dichromate and Mohr salt solution. Dilute solutions are used for these titrations.

7.3 Determination of Dissolved Oxygen in Water: It is one of the important and reliable parameter of condition of water supply for biological, chemical investigations. Sufficient amount of oxygen is required for aquatic life. Oxygen itself is not pollutant for water but its deficiency causes pollution of water. If its concentration is smaller than 4 ppm the water is not suitable aquatic life. Dissolved oxygen in water is essential for bacterial growth also.

7.4 Winkler Azide Method for Determination of DO: This method Involves introducing concentrated solution of $MnSO_4$, NaOH, KI, NaN_3 into water sample. A white precipitates of $Mn(OH)_2$ first formed are oxidised by dissolved oxygen resulting into $Mn(OH)_3$. In presence of sulphuric acid $Mn(OH)_3$ dissolves and liberate oxygen from KI in an amount that is exactly equivalent to dissolved oxygen that is to be titrated with thiosulphate using starch as indicator. The impure sample is refluxed for 2-3 hrs with excess amount of dichromate solution in acidic medium using Ag^+ as catalyst. The excess dichromate is back titrated with standard Mohr's salt. The amount of dichromate used is directly proportional to oxygen required to oxidize the organic matter in the given sample of water.

7.5 Biochemical Oxygen Demand: The BOD value denotes the quantity of oxygen required by the microorganisms to stabilize biologically degradable organic matter in the waste water under aerobic conditions. The BOD is standard means to determine contamination in waste water and sewage water. The BOD value determines

- The pollution load of waste water on environment
- The degree of pollution in lakes and ponds at particular instant.
- Efficiency of treatment plant.
- The value of BOD is expressed in terms of mg/L.

The BOD values are determined with a portion of waste water diluting it with water saturated with oxygen and both immediately and after a period of five days at 20 °C in dark, so that microbes metabolize organic compounds in the waste. The oxygen dissolved in samples is measured before and after incubation.

The Procedure includes the dilution of water first by bubbling compressed air for 1-2 days. To this solution add phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride. If the given solution does not contain microbe add seed for the same. 2-3 ml of sewage water is sufficient for 1000 ml of water. Neutralize the sample to pH 7 with H_2SO_4 if it is alkaline and with NaOH if it is acidic. The sample should be free from residual chlorine before analysis. Make different dilutions of seeded water sample in BOD bottles. Add 1 ml of allyl thiourea solution to each bottle and stopper the bottle immediately, avoid entrapment of air bubbles in BOD bottles. Keep one bottle for immediate determination of DO and other after for 5 days in the dark at 20 °C. The higher temperature is suitable where metabolism rate is high. Prepare a blank in duplicate by making plain dilution of water without seed and measure oxygen consumption in it. Add $MnSO_4$ followed by 2 ml NaOH + KI + NaN_3. titrate the sample=]solution with thiosulphate.

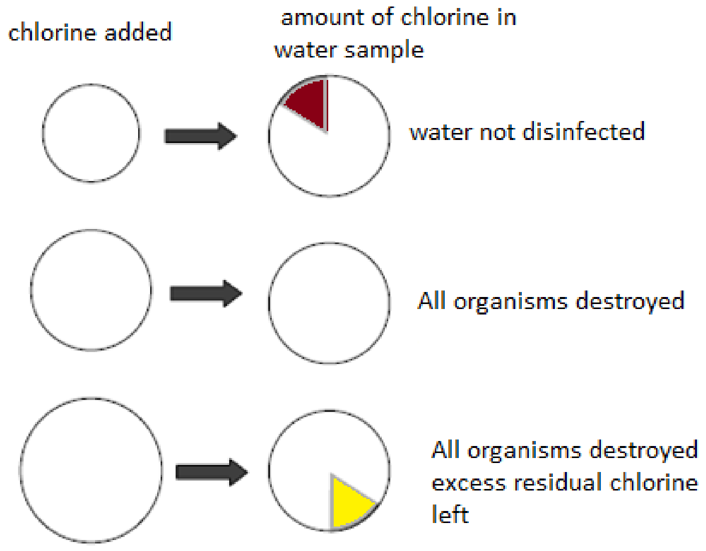
Calculation of BOD of sample as

- D_0 = DO in sample bottle initially
- D_1 = DO in sample bottle on 5th day
- C_0 = DO in blank bottle initially
- C_1 =DO in blank bottle on 5th day
- $(C_0 – C_1)$ = DO depletion in diluted water
- $(D_0 – D_1)$ = DO depletion in sample + dilution water
- $(D_0 – D_1) - (C_0 – C_1)$ = DO depletion due to microbes
- BOD (in ppm or mg/L) = $(D_0 – D_1) - (C_0 – C_1)$ x decimal fraction of sample used.

7.6 Determination of Vitamin C (ascorbic acid): Vitamin C is a colourless, water soluble solid present in many vegetables and citrus fruits and in number of medicines also. The vitamin C content can be determined from given food or medicine with redox titrations. Vitamin C is reducing agent and itself is oxidized. It can be determined by titration with standard iodine solution. Accurately weighed tablet is dissolved in water. To this solution freshly prepared starch solution is added and titrated with standard iodine solution. As vitamin C is easily oxidized by the atmospheric oxygen the titration should be carried out immediately after dissolution.

1 mL of 0.1 N iodine solution = 0.008807 g of ascorbic acid

7.7 Determination of Amount of Residual Chlorine in Water: Chlorine is an important disinfectant that can destroy the pathogenic and other harmful organisms. It can have adverse effect on health. Chlorine may react with humic substances in water to form chlorinated products which can be carcinogenic. At regular intervals residual chlorine should be checked.



Schematic representation showing the importance of test for residual chlorine

The amount of residual chlorine in the sample can be calculated volumetrically using sodium thiosulphate solution using starch as indicator.

$$KI + Cl_2 \qquad 2KCl + I_2$$

$$I_2 \quad + \quad 2Na_2S_2O_3 \qquad\qquad 2NaI \quad + \quad Na_2S_4O_6$$

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