

AN OVERVIEW ON REDOX TITRATIONS

Abstract

Redox reactions occur when both oxidation and reduction take place simultaneously, meaning electrons are transferred from one species to another. In such reactions, there is always a species that gets oxidized and a species that gets reduced, and this exchange of electrons drives the overall chemical transformation. Redox titrations are a type of analytical technique used to determine the concentration of a substance (the analyte) by measuring the quantity of electrons transferred during a redox reaction. Oxidation is a chemical reaction where a substance loses electrons, leading to an increase in its oxidation state. Oxidation can also be defined as the process in which a chemical species loses its "reducing power" or its ability to donate electrons to other substances. Oxidation reactions are often associated with the release of energy, and they are crucial for processes like cellular respiration, where glucose is oxidized to produce energy in the form of ATP. In summary, oxidation and reduction are two complementary processes that involve the transfer of electrons between chemical species, and they are central to numerous natural and industrial processes in the world around us.

Keywords: Reduction, oxidation, Types of redox titration.

Authors

Iram Jahan

IIMT College of Medical Sciences
IIMT University O Pocket
Ganga Nagar, Meerut, India.
Iramjhan1@Gmail.Com

Jiyaul Hak

IIMT College of Medical Sciences
IIMT University O Pocket
Ganga Nagar, Meerut, India.
jiyaultiper@gmail.com

Dr. Nasiruddin Ahmad Farooqui

Translam Institute of Pharmaceutical
Education and Research
Meerut, India.
nasirahmad21@gmail.com

I. REDOX TITRATIONS

Redox titrations are a class of analytical techniques used in chemistry to determine the concentration of a substance (analyte) by measuring the amount of electrons transferred during a redox (reduction-oxidation) reaction. These titrations involve the transfer of electrons between the analyte and a titrant, a known solution of another substance with a known concentration. The reaction between the analyte and titrant is typically monitored using an indicator or an instrument that can detect changes in the system's redox potential. The simplest redox systems are evaluated under static conditions where the focus is on closed systems that are in an equilibrium state. Aqueous bromine solution is an example of such a system (Meija et al., 2017).

Redox reactions involve the exchange of electrons between the species involved. One substance loses electrons (undergoes oxidation) and becomes more positively charged (oxidized), while the other substance gains electrons (undergoes reduction) and becomes more negatively charged (reduced). (Bonomi & Iametti, 2021)
The half-reactions for oxidation and reduction are as follows:

- Oxidation half-reaction: Electrons are lost (an oxidation process).
- Reduction half-reaction: Electrons are gained (a reduction process).

To perform a redox titration, a known volume of the titrant is gradually added to the analyte until the redox reaction is complete. The equivalence point is the stage at which the stoichiometrically correct amount of titrant has been added to react completely with the analyte. At the equivalence point, all the analyte has been oxidized or reduced, and the reaction is balanced according to the stoichiometry of the redox equation.

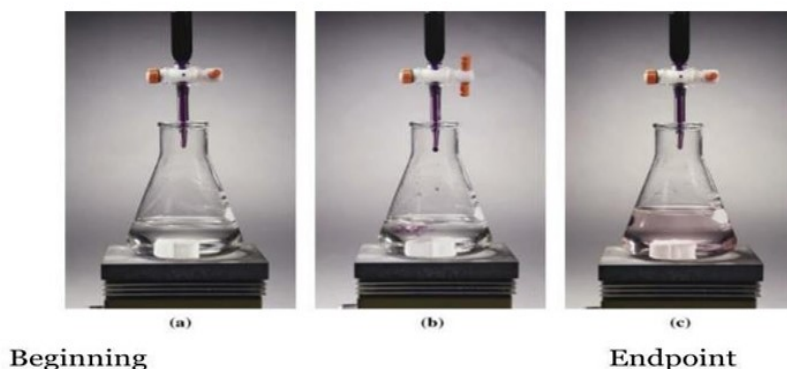


Figure 1: Redox Titration

To detect the equivalence point, an indicator can be used that changes color when the reaction is complete. Alternatively, a potentiometric titration setup can be employed, where the potential difference between the working electrode and reference electrode is monitored as the titrant is added. When the potential levels off, it indicates the equivalence point. (de Levie, 1992).

After the titration, the volume of titrant used is recorded. With the known concentration of the titrant, the number of moles of the analyte present in the original solution can be calculated using the balanced redox equation. From this, the concentration of the analyte can be determined. Redox titrations are used in various applications, such as in the pharmaceutical industry for drug analysis, in environmental monitoring to measure pollutants, and in industrial processes to control the quality of products. The choice of titrant and indicator depends on the specific redox reaction being studied and the properties of the analyte. It's essential to follow proper laboratory techniques and handle chemicals safely during these experiments.

II. CONCEPT OF OXIDATION AND REDUCTION

1. Oxidation and Reduction, often referred to as Redox Reactions, is Fundamental Chemical: processes that involve the transfer of electrons between chemical species. These reactions play a crucial role in various natural and industrial processes, including combustion, metabolism, and corrosion. the specific mechanism of action of the most important representatives of each antioxidant class.(Pisoschi & Pop, 2015)

- **Oxidation:** Oxidation is a chemical reaction where a substance loses electrons, leading to an increase in its oxidation state. In simple terms, it involves the addition of oxygen or the loss of hydrogen or electrons. Oxidation can also be defined as the process in which a chemical species loses its "reducing power" or its ability to donate electrons to other substances. (Barriuso et al., 2013).

The substance being oxidized is called the reducing agent, as it facilitates the oxidation by donating electrons to another species. Oxidation reactions are often associated with the release of energy, and they are crucial for processes like cellular respiration, where glucose is oxidized to produce energy in the form of ATP.

An example of oxidation is the reaction between iron and oxygen to form iron oxide, commonly known as rust: $4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$

In this reaction, iron (Fe) is oxidized to form iron oxide (Fe₂O₃) by losing electrons to oxygen (O₂).

- **Reduction:** Reduction, on the other hand, is a chemical reaction where a substance gains electrons, resulting in a decrease in its oxidation state. This process often involves the addition of hydrogen or electrons or the removal of oxygen from a chemical species. The substance being reduced is called the oxidizing agent, as it facilitates the reduction by accepting electrons from another species. Reduction reactions are associated with the consumption of energy in many cases(Hong et al., 2013).

An example of reduction is the reaction of copper oxide with hydrogen gas to produce copper and water: $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$

In this reaction, copper oxide (CuO) is reduced to form copper (Cu) by gaining electrons from hydrogen (H₂).

2. **Redox Reactions:** Redox reactions occur when both oxidation and reduction take place simultaneously, meaning electrons are transferred from one species to another. In such reactions, there is always a species that gets oxidized and a species that gets reduced, and this exchange of electrons drives the overall chemical transformation.

Redox reactions are essential in various applications, including batteries, fuel cells, and the breakdown of food during digestion. They also play a crucial role in the Earth's atmosphere, where the balance between oxidation and reduction processes influences the concentration of various gases, such as ozone and carbon dioxide. (Hu et al., 2020)

In summary, oxidation and reduction are two complementary processes that involve the transfer of electrons between chemical species, and they are central to numerous natural and industrial processes in the world around us.

III. TYPES OF REDOX TITRATIONS (PRINCIPLE AND APPLICATIONS)

Redox titrations are a type of analytical technique used to determine the concentration of a substance (the analyte) by measuring the quantity of electrons transferred during a redox reaction. These titrations involve the use of an oxidizing agent and a reducing agent to facilitate the electron transfer process. There are several types of redox titrations, each with its own principle and specific applications : (Zhang & Narusawa, 1997)

1. Potassium Permanganate Titrations

- **Principle:** Potassium permanganate (KMnO_4) is a powerful oxidizing agent, and its color changes during the titration from purple to colorless as it is reduced to Mn^{2+} ions. The analyte, typically a reducing agent, is added until it completely reacts with the KMnO_4 , and the endpoint is reached when the purple color disappears.

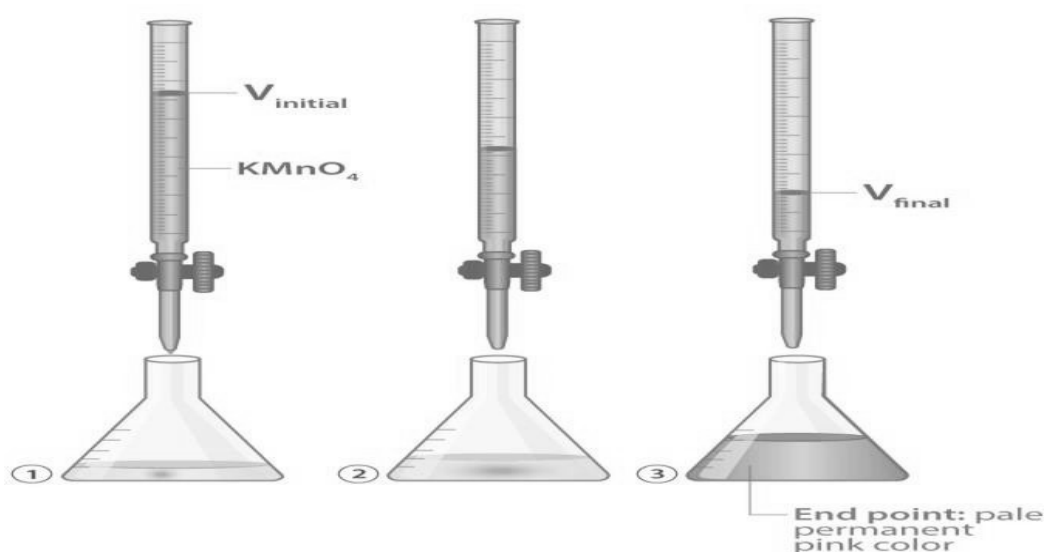


Figure 2: Potassium Permanganate Titrations

- **Applications:** Potassium permanganate titrations are commonly used to determine the concentration of reducing agents like iron, hydrogen peroxide, oxalate ions, and other substances that can be oxidized by KMnO_4 .

2. Iodometric Titrations

- **Principle:** Iodometric titrations involve the use of iodine (I_2) or iodine compounds as the oxidizing agent. The analyte, which is usually a reducing agent, reacts with iodine, converting it to iodide ions (I^-). The endpoint is achieved when all the reducing agent has reacted with iodine and the excess iodine imparts a characteristic color change (e.g., from brown to colorless when using starch as an indicator).
- **Applications:** Iodometric titrations are used to determine the concentration of substances such as vitamin C (ascorbic acid), sulfites, and thiosulfates.

3. Dichromate Titrations

- **Principle:** Dichromate titrations involve the use of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) as an oxidizing agent. The analyte, typically a reducing agent, reacts with dichromate ions, leading to the formation of chromium ions (Cr^{3+}). The color change during the titration from orange to green indicates the endpoint.
- **Applications:** Dichromate titrations are used to determine the concentration of substances like ferrous ions (Fe^{2+}), hydrogen peroxide, and ethanol.

4. Cerium (IV) Sulfate Titrations

- **Principle:** Cerium (IV) sulfate ($\text{Ce}(\text{SO}_4)_2$) acts as an oxidizing agent in these titrations. The analyte, which is a reducing agent, reacts with cerium (IV) ions (Ce^{4+}), reducing them to cerium (III) ions (Ce^{3+}). The endpoint is reached when the excess cerium (IV) ions impart a color change.
- **Applications:** Cerium (IV) sulfate titrations are used to determine the concentration of reducing agents like iron, sulfite ions, and organic compounds containing reducing functional groups.

5. Bromine Titrations

- **Principle:** Bromine (Br_2) is a strong oxidizing agent used in bromine titrations. The analyte, a reducing agent, reacts with bromine, converting it to bromide ions (Br^-). The endpoint is indicated by a color change, such as the disappearance of a red-brown color when using an appropriate indicator.
- **Applications:** Bromine titrations are applied in the determination of reducing agents like phenols, sulfites, and thiosulfates.

These are just a few examples of redox titrations, and there are other variations and applications depending on the specific oxidizing and reducing agents

used, as well as the type of analyte being analyzed. Redox titrations are widely used in quantitative analysis and quality control in various industries, including pharmaceuticals, environmental testing, and chemical manufacturing.

6. Cerimetry: Cerimetry, also known as cerimetric titration or cerimetric analysis, is a type of redox titration method that utilizes cerium (IV) ions (Ce^{4+}) as the titrant. This analytical technique is used to determine the concentration of reducing agents present in a sample. Cerimetry is based on the principle of a redox reaction between the reducing agent in the sample and the cerium (IV) ions. The key components involved in cerimetry are:

- **Titrant:** The titrant is a solution of cerium (IV) ions (Ce^{4+}), which acts as the oxidizing agent. It is prepared by dissolving a known mass of cerium (IV) salt, such as cerium (IV) sulfate ($\text{Ce}(\text{SO}_4)_2$), in a specific volume of a suitable solvent.
- **Indicator:** Cerimetry often employs a visual indicator to determine the endpoint of the titration accurately. Starch is a commonly used indicator in cerimetric titrations. When the cerium (IV) ions are in excess, they form a blue complex with the starch, indicating the endpoint of the titration. The cerimetric titration procedure typically involves the following steps:
- **Preparation of the titrant:** The cerium (IV) solution is prepared by dissolving the cerium (IV) salt in a solvent. The concentration of the titrant should be accurately determined through standardization using a known concentration of a standard reducing agent.
- **Titration process:** A known volume of the sample containing the reducing agent is taken and titrated with the cerium (IV) titrant. As the titration progresses, the cerium(IV) ions react with the reducing agent, resulting in the reduction of cerium(IV) to cerium(III) ions (Ce^{3+}). The endpoint of the titration is indicated by the appearance of a blue color due to the formation of the cerium (IV)-starch complex.
- **Calculation:** The volume of cerium (IV) titrant used is recorded, and the concentration of the reducing agent in the sample is calculated using stoichiometric principles and the known concentration of the cerium (IV) titrant.

Cerimetry is widely used to determine the concentration of various reducing agents in different samples, including analytes such as iron, ascorbic acid (vitamin C), sulfite ions, and reducing sugars. It is a valuable analytical method in fields like chemical analysis, pharmaceuticals, food and beverage industry, and environmental monitoring, where accurate determination of reducing agents is essential. However, it is crucial to handle cerium (IV) solutions carefully, as they can be hazardous and may require specific safety precautions during the titration process.

7. Iodimetry: Iodimetry, also known as iodometric titration or iodometric analysis, is a type of redox titration method that employs iodine (I_2) or iodine compounds as the titrant. This analytical technique is used to determine the concentration of oxidizing agents present in

a sample. Iodimetry is based on the principle of a redox reaction between the oxidizing agent in the sample and the iodine (I₂) or iodide ions (I⁻) in the titrant solution. The key components involved in iodimetry are:

- **Titrant:** The titrant used in iodimetry is a solution containing iodine (I₂) or iodide ions (I⁻). The titrant is typically prepared by dissolving a known mass of iodine or an iodide salt, such as potassium iodide (KI), in a suitable solvent. In some cases, the titrant can be generated in situ by adding a reducing agent to a solution containing iodine, which converts the iodine to iodide ions.
- **Indicator:** To accurately determine the endpoint of the iodometric titration, an appropriate indicator is used. Starch is the most common indicator in iodimetry. When iodine is present in excess, it forms a blue complex with starch, indicating the endpoint of the titration. The iodimetric titration procedure typically involves the following steps:
- **Preparation of the Titrant:** The iodine or iodide solution is prepared by dissolving the iodine or iodide salt in a solvent. The concentration of the titrant should be accurately determined through standardization using a known concentration of a standard oxidizing agent.
- **Titration Process:** A known volume of the sample containing the oxidizing agent is taken and titrated with the iodine or iodide titrant. As the titration progresses, the iodine or iodide reacts with the oxidizing agent, leading to the formation of iodide ions (I⁻). The endpoint of the titration is indicated by the appearance of a blue color due to the formation of the iodine-starch complex.
- **Calculation:** The volume of iodine or iodide titrant used is recorded, and the concentration of the oxidizing agent in the sample is calculated using stoichiometric principles and the known concentration of the iodine or iodide titrant.

Iodimetry is widely used to determine the concentration of various oxidizing agents in different samples, including analytes such as chlorine, hydrogen peroxide, bromine, and nitrites. It is a valuable analytical method in fields like environmental monitoring, water treatment, and pharmaceuticals, where accurate determination of oxidizing agents is essential. However, it is important to handle iodine solutions with care, as they can be toxic and may require specific safety precautions during the titration process.

8. Iodometry: Iodometry, also known as iodometric titration or iodometric analysis, is a type of redox titration method used to determine the concentration of reducing agents present in a sample. Unlike iodimetry, which involves the determination of oxidizing agents using iodine or iodide as the titrant, iodometry utilizes iodine (I₂) or iodine compounds as the oxidizing agent to react with the reducing agent in the sample. The key components involved in iodometry are:

- **Titrant:** The titrant used in iodometry is a solution containing iodine (I₂) or iodine compounds, such as potassium iodate (KIO₃). The titrant is prepared by dissolving a

known mass of iodine or iodate salt in a suitable solvent.

- **Indicator:** An appropriate indicator is used to determine the endpoint of the iodometric titration accurately. Starch is commonly used as an indicator in iodometry. When the iodine is in excess, it forms a blue complex with starch, indicating the endpoint of the titration.
- The iodometric titration procedure typically involves the following steps:
- **Preparation of the Titrant:** The iodine or iodate solution is prepared by dissolving the iodine or iodate salt in a solvent. The concentration of the titrant should be accurately determined through standardization using a known concentration of a standard reducing agent.
- **Sample Preparation:** The sample containing the reducing agent is prepared in a suitable form, and its concentration is either known or needs to be determined.
- **Titration Process:** A known volume of the sample is taken and titrated with the iodine or iodate titrant. As the titration proceeds, the iodine is reduced by the reducing agent in the sample, leading to the formation of iodide ions (I^-). The endpoint of the titration is indicated by the appearance of a blue color due to the formation of the iodine-starch complex.
- **Calculation:** The volume of iodine or iodate titrant used is recorded, and the concentration of the reducing agent in the sample is calculated using stoichiometric principles and the known concentration of the iodine or iodate titrant.

Iodometry is widely used to determine the concentration of various reducing agents in different samples, including analytes such as sulfites, thiosulfates, arsenic, and other substances that can be oxidized by iodine. It is a valuable analytical method in fields like environmental monitoring, water analysis, pharmaceuticals, and food testing, where accurate determination of reducing agents is important. However, it is essential to handle iodine solutions with care, as they can be toxic, and specific safety precautions may be required during the titration process.

9. Bromometry: Bromometry, also known as bromometric titration or bromometric analysis, is a type of redox titration method used to determine the concentration of reducing agents present in a sample. This analytical technique involves the use of bromine (Br_2) or bromine compounds as the titrant, which acts as the oxidizing agent, reacting with the reducing agent in the sample. The key components involved in bromometry are:

- **Titrant:** The titrant used in bromometry is a solution containing bromine (Br_2) or bromine compounds, such as potassium bromate ($KBrO_3$) or bromine water (a solution of bromine in water). The titrant is typically prepared by dissolving a known mass of bromine or bromine compound in a suitable solvent.
- **Indicator:** To accurately determine the endpoint of the bromometric titration, an appropriate indicator is used. Starch is commonly employed as an indicator in

bromometry. When bromine is in excess, it forms a blue complex with starch, indicating the endpoint of the titration. The bromometric titration procedure typically involves the following steps:

- **Preparation of the Titrant:** The bromine or bromine compound solution is prepared by dissolving the bromine or bromine compound in a solvent. The concentration of the titrant should be accurately determined through standardization using a known concentration of a standard reducing agent.
- **Sample Preparation:** The sample containing the reducing agent is prepared in a suitable form, and its concentration is either known or needs to be determined.
- **Titration Process:** A known volume of the sample is taken and titrated with the bromine or bromine compound titrant. As the titration progresses, the bromine is reduced by the reducing agent in the sample, leading to the formation of bromide ions (Br^-). The endpoint of the titration is indicated by the appearance of a blue color due to the formation of the bromine-starch complex.
- **Calculation:** The volume of bromine or bromine compound titrant used is recorded, and the concentration of the reducing agent in the sample is calculated using stoichiometric principles and the known concentration of the bromine or bromine compound titrant.

Bromometry is widely used to determine the concentration of various reducing agents in different samples, including analytes such as sulfites, thiosulfates, and other substances that can be oxidized by bromine. It is a valuable analytical method in fields like environmental monitoring, water analysis, pharmaceuticals, and chemical manufacturing, where accurate determination of reducing agents is crucial. However, it is important to handle bromine solutions with care, as they can be hazardous and may require specific safety precautions during the titration process.

10. Dichrometry and Titration with Potassium –Iodate: Dichrometry is a type of redox titration method used to determine the concentration of reducing agents present in a sample. This analytical technique involves the use of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) as the titrant, which acts as the oxidizing agent, reacting with the reducing agent in the sample. (Rao & Rao, 1956) The key components involved in dichrometry are:

- **Titrant:** The titrant used in dichrometry is a solution containing potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). The titrant is typically prepared by dissolving a known mass of potassium dichromate in a suitable solvent.
- **Indicator:** To accurately determine the endpoint of the dichrometric titration, an appropriate indicator is used. The indicator used in dichrometry is often a visual one, such as a color change, to detect the endpoint. In some cases, a separate indicator solution may not be needed, and the titration can be self-indicating based on the color changes during the titration process.

- **Preparation of the Titrant:** The potassium dichromate solution is prepared by dissolving the potassium dichromate in a solvent. The concentration of the titrant should be accurately determined through standardization using a known concentration of a standard reducing agent.
- **Sample Preparation:** The sample containing the reducing agent is prepared in a suitable form, and its concentration is either known or needs to be determined.
- **Titration Process:** A known volume of the sample is taken and titrated with the potassium dichromate titrant. As the titration progresses, the potassium dichromate is reduced by the reducing agent in the sample, leading to the formation of chromium ions (Cr^{3+}). The endpoint of the titration is indicated by a color change, such as from orange to green, when using potassium dichromate as the visual indicator.
- **Calculation:** The volume of potassium dichromate titrant used is recorded, and the concentration of the reducing agent in the sample is calculated using stoichiometric principles and the known concentration of the potassium dichromate titrant.

11. Titration with Potassium Iodate: Potassium iodate (KIO_3) is used as a primary standard in titrations. In a titration involving potassium iodate, the iodate ions are reduced to iodine (I_2) by the reducing agent present in the sample. The iodine formed is then titrated with a standard solution of a reducing agent, typically sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), in the presence of a starch indicator. The titration with potassium iodate involves the following steps:

- **Preparation of Standard Sodium Thiosulfate Solution:** A standard solution of sodium thiosulfate is prepared, and its concentration is accurately determined by standardization against a primary standard of potassium iodate.
- **Sample Preparation:** The sample containing the reducing agent is prepared in a suitable form, and its concentration is either known or needs to be determined.
- **Titration Process:** A known volume of the sample is taken and titrated with the potassium iodate solution. The potassium iodate reacts with the reducing agent in the sample, producing iodine. The iodine formed is then titrated with the standard sodium thiosulfate solution until the endpoint is reached. The endpoint is indicated by the appearance of a pale yellow color when the iodine-starch complex forms.
- **Calculation:** The volume of potassium iodate titrant used and the volume of sodium thiosulfate titrant used are recorded, and the concentration of the reducing agent in the sample is calculated using stoichiometric principles and the known concentration of the sodium thiosulfate titrant.

Titration with potassium iodate is commonly used to determine the concentration of reducing agents like sulfites, thiosulfates, and other substances capable of reducing iodate ions to iodine. It is a valuable analytical method in various fields, including environmental testing, water analysis, food and beverage industry, and chemical manufacturing.

IV. CONCLUSION

The conclusion of a redox titration is a summary of the results obtained from the experiment, highlighting the key findings and their implications. It is essential to be clear and concise, emphasizing the determined concentration of the unknown species and the accuracy of the results. Here's a step-by-step guide to writing the conclusion of a redox titration: State the Objective, Present the Results, Discuss the Calculations, Interpret the Results. The conclusion should be based solely on the data and results obtained during the experiment. Avoid introducing new information or discussing concepts that were not part of the original experiment. Be objective and stick to the facts while providing a clear and logical summary of the redox titration results.

REFERENCES

- [1] Barriuso, B., Astiasarán, I., & Ansorena, D. (2013). A review of analytical methods measuring lipid oxidation status in foods: A challenging task. In *European Food Research and Technology*. <https://doi.org/10.1007/s00217-012-1866-9>
- [2] Bonomi, F., & Iametti, S. (2021). Redox Titration of Flavoproteins: An Overview. In *Methods in Molecular Biology*. https://doi.org/10.1007/978-1-0716-1286-6_8
- [3] de Levie, R. (1992). A simple expression for the redox titration curve. *Journal of Electroanalytical Chemistry*. [https://doi.org/10.1016/0022-0728\(92\)80022-V](https://doi.org/10.1016/0022-0728(92)80022-V)
- [4] Hong, J., Zhang, W., Ren, J., & Xu, R. (2013). Photocatalytic reduction of CO₂: A brief review on product analysis and systematic methods. In *Analytical Methods*. <https://doi.org/10.1039/c2ay26270c>
- [5] Hu, A., Zhou, M., Lei, T., Hu, Y., Du, X., Gong, C., Shu, C., Long, J., Zhu, J., Chen, W., Wang, X., & Xiong, J. (2020). Optimizing Redox Reactions in Aprotic Lithium–Sulfur Batteries. In *Advanced Energy Materials*. <https://doi.org/10.1002/aenm.202002180>
- [6] Meija, J., Michałowska-Kaczmarczyk, A. M., & Michałowski, T. (2017). Redox titration challenge. *Analytical and Bioanalytical Chemistry*. <https://doi.org/10.1007/s00216-016-0020-0>
- [7] Pisoschi, A. M., & Pop, A. (2015). The role of antioxidants in the chemistry of oxidative stress: A review. In *European Journal of Medicinal Chemistry*. <https://doi.org/10.1016/j.ejmech.2015.04.040>
- [8] Rao, G. G., & Rao, K. B. (1956). Dichrometric estimation of phosphite and hypophosphite silver salt catalysis. *Fresenius' Zeitschrift Für Analytische Chemie*. <https://doi.org/10.1007/BF00535375>
- [9] Zhang, C. L., & Narusawa, Y. (1997). A New Titration Method Based on Concentration- Variable Patterns. Principles and Applications to Acid-Base and Redox Titrations. *Bulletin of the Chemical Society of Japan*. <https://doi.org/10.1246/bcsj.70.593>