

DEVELOPMENT AND ANALYTICAL PERFORMANCE OF SILVER-BASED INORGANIC ANION SELECTIVE INDICATOR

SANDHYA

Research Scholar,
Department of Chemistry,
Singhania University, Pacheri Bari,
Jhunjhunu, Rajasthan.

DR. YOGESH KUMAR

Department of Chemistry,
Singhania University, Pacheri Bari,
Jhunjhunu, Rajasthan.

ABSTRACT

Silver-based inorganic anion selective indicator electrodes have emerged as reliable electrochemical sensors for the rapid and accurate determination of various inorganic anions in chemical, environmental, and industrial samples. The present study focuses on the fabrication, optimization, and analytical evaluation of silver-based indicator electrodes for the detection of bromide, iodide, cyanide, and thiocyanate ions. Different fabrication techniques, including PVC membrane, silicone grease, coated wire, and pellet methods, are compared to identify the most efficient electrode preparation strategy. The analytical performance of the developed electrodes is evaluated in terms of sensitivity, selectivity, response time, reproducibility, durability, detection limit, and Nernstian behavior. The influence of pH, temperature, ionic strength, and interfering ions on electrode performance is also investigated. Thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) are determined to understand the electrochemical behavior of the electrodes. Statistical analysis is performed to validate the experimental results. The findings are expected to contribute to the development of cost-effective, stable, and highly selective ion-selective electrodes for electrochemical analysis, environmental monitoring, and quality control in the chemical industry.

Keywords: Silver-based electrodes; Ion-selective electrodes; Inorganic anions; Potentiometric analysis; Electrochemical sensors; Silver halide electrodes; Membrane electrodes; Analytical performance; Chemical industry; Electrochemical characterization.

INTRODUCTION

Electrochemistry is a fundamental branch of chemistry that deals with the interconversion of chemical and electrical energy through oxidation–reduction (redox) reactions. It plays a crucial role in understanding electron transfer processes and has become an indispensable tool in analytical chemistry, materials science, environmental monitoring, and industrial process control. Electrochemical techniques are widely employed for the qualitative and quantitative determination of chemical species because they offer high sensitivity, rapid response, simplicity of operation, and cost-effectiveness. Among these techniques, potentiometric analysis using ion-selective electrodes (ISEs) has gained significant importance due to its ability to selectively detect specific ions in complex sample matrices.

Ion-selective electrodes are electrochemical sensors that generate an

electrical potential proportional to the activity of a particular ion in solution. These electrodes operate on the principle of selective ion exchange across a membrane, resulting in a measurable potential difference that follows the Nernst equation. Their high selectivity, fast response, minimal sample preparation, and non-destructive nature make them valuable tools in chemical laboratories, environmental analysis, pharmaceutical quality control, food industries, and clinical diagnostics. Continuous developments in membrane materials and electrode fabrication techniques have further enhanced their analytical performance and broadened their industrial applications.

Silver-based inorganic anion selective indicator electrodes constitute an important class of ion-selective electrodes specifically designed for the determination of inorganic anions such as bromide (Br^-), iodide (I^-), cyanide (CN^-), and thiocyanate (SCN^-). These electrodes generally employ sparingly soluble silver salts as electroactive membrane materials, which exhibit high affinity and selectivity toward their corresponding anions. The electrode potential developed at the membrane-solution interface is directly related to the activity of the target anion, allowing accurate potentiometric measurements over a wide concentration range. Because of their excellent sensitivity, reproducibility, and operational simplicity, silver-based electrodes are extensively used in analytical chemistry for potentiometric titrations and direct ion determination.

The analytical performance of an ion-selective electrode depends largely on its fabrication method and membrane composition. Various preparation techniques, including PVC membrane, silicone grease, coated-wire, and pellet methods, have been developed to improve electrode stability, mechanical strength, response time, and selectivity. Each fabrication technique offers distinct advantages and limitations regarding membrane homogeneity, electrical conductivity, durability, and long-term performance. Therefore, systematic comparison of these methods is essential for identifying the most suitable approach for developing reliable and efficient indicator electrodes for routine analytical applications.

The performance of silver-based anion selective electrodes is influenced by several experimental parameters, including solution pH, temperature, ionic strength, and the presence of interfering ions. These factors affect membrane equilibrium and ion transport, thereby influencing electrode sensitivity, selectivity, and accuracy. Consequently, optimization of operating conditions is necessary to achieve Nernstian response, low detection limits, and stable electrode potentials. In addition, thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) provide valuable insights into the energetics of ion-selective processes and contribute to a better understanding of electrode behavior under different experimental conditions.

The increasing demand for rapid, accurate, and economical analytical techniques in the chemical industry has further enhanced the significance of ion-selective electrode technology. Silver-based anion selective electrodes can be employed for process monitoring, quality assurance, environmental pollution control, wastewater analysis, and industrial product testing. Their ability to provide real-time measurements without extensive sample preparation makes them highly suitable for continuous industrial monitoring and automated analytical systems. Moreover, these electrodes contribute to reducing analytical costs while maintaining high precision and reliability.

In recent years, advances in electrochemical sensor technology have focused on improving the selectivity, durability, and miniaturization of ion-selective electrodes through the use of novel membrane materials, nanostructured composites, and advanced

fabrication methods. These developments have expanded the scope of electrochemical sensors in modern analytical science and industrial applications. However, comparative studies evaluating different fabrication techniques for silver-based inorganic anion selective indicator electrodes under identical experimental conditions remain limited.

The present study aims to develop and systematically evaluate silver-based inorganic anion selective indicator electrodes prepared by different fabrication methods. Their analytical performance will be assessed in terms of sensitivity, selectivity, response time, reproducibility, stability, detection limit, and operational lifetime. The effects of pH, temperature, ionic strength, and interfering ions will also be investigated, along with thermodynamic and statistical analyses of the obtained data. The findings of this study are expected to contribute to the development of robust, accurate, and cost-effective electrochemical sensors suitable for analytical laboratories and the chemical industry, thereby enhancing the efficiency and reliability of modern electrochemical analysis.

LITERATURE REVIEW

The scientific development of electrochemistry began with the investigations of Cavendish, who studied the electrical conductivity of aqueous solutions. Galvani (1791) examined electrical phenomena in animal tissues, while Volta's subsequent experiments established that electricity could be generated through the interaction of metals and electrolytes. Nicholson and Carlisle (1800) demonstrated the electrolysis of water, whereas Davy (1808) used electrical current for the decomposition of aqueous solutions and moist alkalis.

Oersted (1820) established the relationship between electricity and magnetism. Daniell (1836) developed a two-fluid cell that provided a stable electrical current and reduced polarization. Grove (1839) constructed an early fuel cell, while Bunsen (1841) replaced the costly platinum electrode with carbon, improving its practical applicability.

Hittorf (1853) demonstrated that ions move at different rates in electrolyte solutions and introduced the concept of ionic transport numbers. Clausius (1857) suggested that charged particles already exist in electrolyte solutions. Between 1875 and 1879, Kohlrausch developed the law of independent migration of ions and employed alternating current for accurate conductivity measurements.

Arrhenius (1887) proposed the theory of electrolytic dissociation, explaining that electrolytes dissociate into positively and negatively charged ions in solution. Nernst (1888) established a mathematical relationship between electrode potential, temperature and ionic activity. The Nernst equation later became the theoretical foundation of potentiometric and ion-selective electrode measurements.

Noyes (1904) provided experimental evidence supporting the extensive ionization of strong electrolytes. The crystal-structure investigations of Bragg and Bragg (1928, 1934) further confirmed the ionic nature of crystalline compounds. These studies strengthened the theoretical basis of solid-state and precipitate-based electrodes.

Marshall and Bergman (1941) investigated clay membranes for ionic measurements. Leden (1941, 1944) employed potentiometric methods for studying metal complexes, particularly cadmium–cyanide systems. Hall and Young (1946) examined cyanide and fluoride complexes through potentiometric measurements.

Allen and Hickling (1957) investigated electrode potentials in alkaline sulphide and polysulphide solutions using platinum, tungsten, graphite, nickel and gold electrodes. Their study contributed to the understanding of sulphide-ion electrode reactions. Reilley and

Schmid (1958) developed a mercury–mercury EDTA complex electrode for identifying equivalence points in complexometric titrations.

Gavriş (1960) proposed a potentiometric method for the determination of xanthates by using silver nitrate and thioacetamide. Mukherjee (1961) used clay plugs for measuring the activities of alkali and alkaline-earth ions. Clark and Lyons (1962) introduced an enzyme electrode for glucose determination, thereby expanding potentiometric sensing into biochemical analysis.

Katz and Rechnitz (1963) studied membrane electrodes for selective ionic determination. Pungor, Havas and Toth (1964–1965) developed precipitate-based ion-selective electrodes containing sparingly soluble metal salts. Their research demonstrated the usefulness of solid-state membranes for selective potentiometric measurements.

Popa and Magearu (1969) employed silver–silver ligand electrodes to investigate complexes of zinc, cadmium, cobalt and nickel. During the same period, Baumann and Wallace (1969) and Ross and Frant (1969) reported important developments in solid-state and membrane-based ion-selective electrodes.

Ruzicka and Lamm (1971) investigated the analytical behaviour of ion-selective electrodes and contributed to the development of potentiometric measurement techniques. James, Carmack and Freiser (1972) examined the analytical response of membrane electrodes, while Paperiello, Mukherji and Shearer (1973) studied their selectivity and practical applications.

Hulanicki and Trojanowicz (1973) evaluated membrane electrodes for analytical determinations and emphasized the importance of electrode selectivity. Stetiu and Cormos (1975) investigated lead sulphide crystal electrodes for determining sulphide, lead, copper, mercury and silver ions at relatively low concentrations.

Vande Leest (1977) examined mixed-metal sulphide membranes and studied the relationship between membrane structure and electrochemical behaviour. The effects of chloride, nitrate, carbonate and complexing agents on electrode response were also evaluated.

Tanaka and co-workers (1978–1985) developed ion-selective electrodes for phosphate and arsenate ions using water-insoluble lead compounds as membrane components. Their work showed that sparingly soluble inorganic materials could be effectively employed in anion-selective membranes.

Cammann (1979) systematically described the principles, construction, calibration and analytical applications of ion-selective electrodes. His work established ion-selective potentiometry as a practical technique for laboratory and industrial analysis.

Bühlmann, Pretsch and Bakker (1998) reviewed carrier-based ion-selective electrodes and explained the importance of ionophores, membrane composition and ion-transfer equilibria in determining electrode selectivity and sensitivity.

During the early twenty-first century, research increasingly focused on lowering the detection limits of anion-selective electrodes. A 2002–2003 study showed that optimization of the internal solution and membrane composition could significantly improve the detection limit and selectivity of anion-sensitive electrodes.

Research on solid-contact electrodes demonstrated that removing the internal filling solution could produce compact, mechanically stable and portable potentiometric sensors. A 2005 study reported that properly designed solid-contact electrodes could offer rapid response, high reproducibility and improved operational stability.

Zdrachek and Bakker (2018) reviewed developments in potentiometric sensing

between 2016 and 2018. They highlighted progress in solid-contact electrodes, miniaturized sensors, membrane optimization, trace-level analysis and practical applications of potentiometric devices.

A theoretical investigation published in 2018 examined the sensitivity and selectivity of plastic-membrane ion-selective electrodes through the Nernst–Planck–Poisson model. The study showed that membrane transport, ionic interactions and boundary conditions considerably influence electrode response.

In 2020, direct potentiometric sensing was further examined for the determination of anion activity. The study emphasized that ion-selective electrodes respond primarily to ionic activity rather than simple analytical concentration. It also demonstrated the continuing relevance of potentiometric sensors for rapid and direct anion measurement.

The reviewed studies show that silver salts such as silver bromide, silver iodide, silver cyanide and silver thiocyanate possess suitable electrochemical characteristics for constructing inorganic anion-selective indicator electrodes. However, comparatively fewer studies have evaluated these electrodes prepared through PVC membrane, silicone grease, coated-wire and pellet methods under identical experimental conditions.

Therefore, the present study seeks to develop silver-based inorganic anion-selective electrodes and compare their analytical performance in terms of Nernstian slope, concentration range, detection limit, response time, reproducibility, durability, pH dependence, temperature dependence and interference from other ions. Such a comparative study may support the development of economical and reliable potentiometric sensors for chemical-industry and environmental applications.

MATERIALS AND METHODS

* Materials

Analytical reagent (AR) grade chemicals were used throughout the study without further purification. Silver nitrate (AgNO_3), potassium bromide (KBr), potassium iodide (KI), potassium cyanide (KCN), potassium thiocyanate (KSCN), polyvinyl chloride (PVC), silicone grease, tetrahydrofuran (THF), graphite powder, and other laboratory reagents were procured from standard chemical suppliers. Double-distilled water was used for the preparation of all solutions.

* Preparation of Indicator Electrodes

Silver-based inorganic anion selective indicator electrodes were prepared using four different fabrication techniques:

- **PVC Membrane Method:** A membrane containing the electroactive silver salt was prepared by mixing PVC, plasticizer, and the active material. The membrane was cast, dried, and fixed onto the electrode body.
- **Silicone Grease Method:** The electroactive silver compound was uniformly mixed with silicone grease to prepare a homogeneous membrane, which was then mounted on the electrode surface.
- **Coated Wire Method:** A cleaned silver wire was repeatedly coated with the membrane mixture and allowed to dry until a uniform sensing layer was obtained.
- **Pellet Method:** Finely powdered electroactive material was compressed under high pressure to prepare a solid pellet, which served as the sensing membrane.

* Electrochemical Measurements

The prepared electrodes were conditioned in the corresponding anion solution before use. Potentiometric measurements were carried out using a digital pH/mV meter at

room temperature with a saturated calomel electrode (SCE) or Ag/AgCl electrode as the reference electrode. Standard solutions of bromide, iodide, cyanide, and thiocyanate ions were prepared in the concentration range of 10^{-1} – 10^{-7} M.

* Evaluation of Analytical Performance

The analytical performance of each electrode was evaluated using the following parameters:

- * Calibration curve
- * Nernstian slope
- * Linear working concentration range
- * Detection limit
- * Response time
- * Reproducibility
- * Repeatability
- * Operational lifetime (durability)
- * Selectivity towards target anions

* Effect of Experimental Variables

The influence of different experimental conditions on electrode performance was investigated:

Effect of pH: The electrode potential was measured over a suitable pH range to determine the optimum working pH.

Effect of Temperature: Measurements were performed at different temperatures to study thermal stability and temperature dependence.

Effect of Ionic Strength: The influence of ionic strength on electrode response was evaluated using suitable supporting electrolytes.

Interference Study: The selectivity of the electrodes was examined in the presence of common interfering inorganic ions.

* Thermodynamic Studies

Thermodynamic parameters including Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated from the experimental data obtained at different temperatures to evaluate the electrochemical behaviour of the prepared electrodes.

* Statistical Analysis

The experimental results were statistically analysed to assess the reliability and precision of the developed electrodes. Mean, standard deviation (SD), relative standard deviation (RSD), regression coefficient (R^2), and percentage error were calculated. Calibration plots were used to determine the linearity of the electrode response, and comparative statistical analysis was performed to identify the most effective electrode preparation method.

* Flow of Experimental Work

Preparation of reagents → Fabrication of silver-based indicator electrodes → Electrode conditioning → Calibration → Potentiometric measurements → Evaluation of analytical performance → Effect of pH, temperature and interfering ions → Thermodynamic calculations → Statistical analysis → Interpretation of results.

ANALYTICAL PERFORMANCE EVALUATION

The analytical performance of the developed silver-based inorganic anion selective indicator electrodes was evaluated to determine their suitability for potentiometric

analysis. The electrodes prepared by different fabrication methods (PVC membrane, silicone grease, coated wire, and pellet method) were compared using standard electrochemical performance parameters.

* **Calibration Characteristics**

Calibration curves were constructed by measuring the electrode potential in standard solutions of bromide, iodide, cyanide, and thiocyanate ions over a wide concentration range (10^{-1} – 10^{-7} M). The linear relationship between electrode potential and the logarithm of ion concentration was examined according to the Nernst equation.

* **Sensitivity and Nernstian Response**

The sensitivity of each electrode was determined from the slope of the calibration curve. The experimental slopes were compared with the theoretical Nernstian value to assess the electrochemical performance and efficiency of the fabricated electrodes.

* **Detection Limit and Linear Working Range**

The minimum detectable concentration and the linear concentration range of each electrode were determined. These parameters indicate the applicability of the electrodes for trace-level and routine analytical measurements.

* **Response Time**

The response time was measured as the time required for the electrode potential to reach a stable value after transferring the electrode from one concentration to another. A shorter response time indicates better analytical performance.

* **Reproducibility and Repeatability**

The reproducibility of the electrode response was evaluated by repeated measurements under identical experimental conditions. Repeatability was assessed through successive measurements of standard solutions, and the results were expressed as standard deviation (SD) and relative standard deviation (RSD).

* **Selectivity**

The selectivity of the developed electrodes towards their respective target anions was investigated in the presence of common interfering ions. Selectivity coefficients were calculated to evaluate the influence of foreign ions on electrode response.

* **Stability and Durability**

The long-term stability and operational lifetime of the electrodes were examined by recording their responses over an extended period. Any drift in electrode potential and deterioration in analytical performance were carefully monitored.

EFFECT OF EXPERIMENTAL PARAMETERS

The performance of ion-selective electrodes is strongly influenced by experimental conditions. Therefore, the effects of different operating parameters were systematically investigated.

* **Effect of pH**

The electrode potential was measured over a suitable pH range to determine the optimum working pH. The study identified the pH range in which the electrode exhibited stable and Nernstian behaviour without significant interference from hydrogen or hydroxide ions.

* **Effect of Temperature**

Electrode responses were recorded at different temperatures to evaluate thermal stability and temperature dependence. Changes in electrode potential with

temperature were analysed to assess the influence of thermal conditions on analytical performance.

*** Effect of Ionic Strength**

The influence of ionic strength on electrode response was studied by using supporting electrolytes of different concentrations. Maintaining constant ionic strength ensured reliable and reproducible potentiometric measurements.

*** Effect of Interfering Ions**

The effect of commonly occurring inorganic ions such as chloride, nitrate, sulphate, carbonate and phosphate on electrode response was investigated. The selectivity of the developed electrodes was evaluated by comparing the potential obtained in the presence and absence of interfering ions.

*** Medium Dependence**

The behaviour of the electrodes was examined in different aqueous media to determine their suitability under varying analytical conditions. The effect of solvent composition on electrode potential and analytical performance was also evaluated.

*** Optimization of Experimental Conditions**

Based on the experimental observations, the optimum operating conditions—including pH, temperature, ionic strength and measurement medium—were established to achieve maximum sensitivity, selectivity, stability and reproducibility of the developed silver-based inorganic anion selective indicator electrodes.

THERMODYNAMIC AND STATISTICAL ANALYSIS

*** Thermodynamic Analysis**

The thermodynamic behaviour of the developed silver-based inorganic anion selective indicator electrodes was investigated to understand the electrochemical processes occurring at the electrode–solution interface. Electrode potentials were measured at different temperatures under equilibrium conditions. The experimental data were used to evaluate the thermodynamic parameters, namely Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS).

The Gibbs free energy change (ΔG) was calculated to determine the spontaneity of the electrochemical reaction. The enthalpy change (ΔH) was estimated from the temperature dependence of electrode potential, while the entropy change (ΔS) was calculated to evaluate the degree of randomness associated with the ion–electrode interaction. These thermodynamic parameters provided valuable information regarding the stability and electrochemical performance of the prepared electrodes.

The effect of temperature on the electrode response was also examined to determine the optimum operating temperature and to evaluate the thermal stability of the developed electrodes. The results were compared for electrodes prepared by different fabrication methods to identify the most thermodynamically stable electrode system.

*** Statistical Analysis**

Statistical analysis was performed to assess the precision, accuracy, and reliability of the experimental data obtained from the developed electrodes. All potentiometric measurements were carried out in triplicate, and the results were expressed as mean $\pm$ standard deviation (SD).

The reproducibility of the electrodes was evaluated using the relative standard deviation (RSD), while calibration data were analysed by linear regression analysis to determine the correlation coefficient (R^2), slope, and intercept. The percentage error was also

calculated to evaluate the analytical accuracy of the developed electrodes.

Comparative statistical analysis was performed to assess the analytical performance of the electrodes prepared by PVC membrane, silicone grease, coated-wire, and pellet methods. The statistical parameters were used to identify the fabrication method that provided the best sensitivity, reproducibility, stability, and overall analytical performance.

The combined thermodynamic and statistical analyses enabled a comprehensive evaluation of the developed silver-based inorganic anion selective indicator electrodes and established their suitability for potentiometric analysis in chemical and industrial applications.

RESULTS AND DISCUSSION

The present study focused on the development and analytical evaluation of silver-based inorganic anion selective indicator electrodes prepared by four different fabrication techniques, namely PVC membrane, silicone grease, coated-wire, and pellet methods. The experimental results obtained from calibration studies, response characteristics, thermodynamic investigations, and statistical analysis were compared to identify the most suitable electrode preparation method.

*** Comparative Performance of Different Fabrication Methods**

The fabricated electrodes exhibited satisfactory potentiometric responses toward bromide, iodide, cyanide, and thiocyanate ions. However, noticeable differences were observed in terms of sensitivity, response time, reproducibility, and operational stability. Among the four preparation methods, the PVC membrane and pellet electrodes showed superior analytical performance owing to their better membrane homogeneity, mechanical stability, and longer operational lifetime. The coated-wire electrodes demonstrated rapid response but exhibited comparatively higher potential drift during prolonged use. Silicone grease electrodes provided acceptable sensitivity but showed relatively lower durability than PVC membrane and pellet electrodes.

*** Calibration Characteristics and Electrode Response**

Calibration plots showed a linear relationship between electrode potential and the logarithm of anion concentration within the selected working range. The developed electrodes exhibited nearly Nernstian behaviour, indicating efficient ion exchange at the membrane–solution interface. The linear response confirmed that the fabricated electrodes could be successfully employed for quantitative potentiometric determination of inorganic anions over a wide concentration range.

*** Detection Limit and Response Time**

The detection limits obtained for the developed electrodes were sufficiently low for routine laboratory and industrial analysis. The response time of the electrodes ranged from a few seconds to less than one minute depending on the fabrication method and analyte concentration. PVC membrane and coated-wire electrodes attained stable potentials more rapidly than the other fabricated electrodes, making them suitable for rapid analytical measurements.

*** Effect of Experimental Parameters**

The electrode response remained stable within an optimum pH range, while deviations were observed under highly acidic or alkaline conditions due to changes in ionic activity and membrane equilibrium. Temperature studies indicated a slight increase in

electrode potential with increasing temperature, consistent with electrochemical theory. Constant ionic strength improved the reproducibility of measurements, whereas common interfering ions produced only minor effects on the selectivity of the optimized electrodes.

*** Thermodynamic Behaviour**

Thermodynamic analysis indicated that the electrode reactions were thermodynamically favourable under the selected experimental conditions. The calculated values of Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) confirmed the stability of the electrode systems and supported the spontaneous ion-exchange processes occurring at the membrane surface. Temperature-dependent studies further demonstrated that the developed electrodes maintained stable electrochemical performance over the investigated temperature range.

*** Statistical Interpretation**

The statistical evaluation revealed low standard deviation (SD) and relative standard deviation (RSD) values, indicating excellent precision and reproducibility of the developed electrodes. Regression analysis produced correlation coefficients (R^2) close to unity, confirming the linearity of the calibration curves. These findings demonstrate the reliability of the fabricated electrodes for quantitative electrochemical analysis.

*** Comparison with Previous Studies**

The analytical performance of the developed electrodes was found to be comparable with previously reported silver-based ion-selective electrodes. The optimized electrodes exhibited satisfactory sensitivity, rapid response, good selectivity, and excellent stability. The comparative evaluation of different fabrication methods showed that membrane composition and preparation technique significantly influenced electrode performance. The findings are in agreement with earlier studies reporting that PVC membrane and pellet-type electrodes generally provide superior analytical characteristics compared with conventional coated-wire and grease-based electrodes.

*** Industrial Significance**

The developed silver-based inorganic anion selective indicator electrodes have considerable potential for practical applications in the chemical industry. Their rapid response, good selectivity, low cost, and ease of fabrication make them suitable for quality control, industrial process monitoring, environmental analysis, wastewater testing, and routine laboratory investigations. The optimized electrodes can serve as reliable electrochemical sensors for the determination of bromide, iodide, cyanide, and thiocyanate ions in various industrial and environmental samples.

Overall, the experimental results demonstrate that the developed silver-based inorganic anion selective indicator electrodes possess satisfactory analytical characteristics and can be effectively employed for accurate, rapid, and economical potentiometric analysis in chemical and industrial applications.

APPLICATIONS

Silver-based inorganic anion selective indicator electrodes have wide applications in analytical chemistry, environmental monitoring, industrial process control, and quality assurance. Their high selectivity, rapid response, low cost, and ease of operation make them suitable for routine laboratory as well as industrial analysis.

*** Chemical Industry**

The developed electrodes can be used for the determination of bromide, iodide, cyanide, and thiocyanate ions during the manufacturing of chemicals, dyes, pharmaceuticals, fertilizers, and electroplating solutions. They provide rapid and reliable

monitoring of process streams, helping to improve product quality and production efficiency.

*** Environmental Monitoring**

Silver-based indicator electrodes are useful for the analysis of inorganic anions in surface water, groundwater, industrial effluents, and wastewater. They assist in monitoring environmental pollution and ensuring compliance with environmental quality standards.

*** Water Quality Analysis**

The developed electrodes can be employed for routine determination of inorganic anions in drinking water, river water, and industrial water supplies. Their rapid response and high sensitivity make them suitable for continuous water quality assessment.

*** Pharmaceutical and Clinical Analysis**

These electrodes can be applied in pharmaceutical quality control for the determination of halide ions in pharmaceutical formulations and raw materials. They may also be used in selected clinical and biochemical analyses where specific inorganic ions require accurate measurement.

*** Potentiometric Titrations**

Silver-based indicator electrodes serve as efficient indicator electrodes in precipitation and potentiometric titrations involving halides, cyanide, thiocyanate, and other inorganic anions. They provide accurate endpoint detection without the need for visual indicators.

*** Research and Educational Laboratories**

The developed electrodes are valuable tools for electrochemical research, analytical chemistry experiments, and teaching laboratories. They are widely used for studying electrode behaviour, ion-selective membrane characteristics, and electrochemical equilibrium.

*** Food and Agricultural Analysis**

These electrodes can be used for monitoring inorganic anions in food products, agricultural chemicals, fertilizers, and irrigation water to ensure product quality and environmental safety.

*** Future Prospects**

Advances in membrane materials, nanotechnology, and solid-contact electrode design are expected to further improve the sensitivity, selectivity, stability, and portability of silver-based inorganic anion selective indicator electrodes. These developments will expand their applications in real-time industrial process monitoring, environmental surveillance, biomedical diagnostics, and automated analytical systems.

Overall, the developed silver-based inorganic anion selective indicator electrodes offer a simple, rapid, economical, and reliable analytical tool for the determination of inorganic anions and have significant potential for applications in modern chemical industries, environmental monitoring, and analytical laboratories.

CONCLUSION

The present study successfully demonstrated the development and analytical evaluation of silver-based inorganic anion selective indicator electrodes for the determination of bromide, iodide, cyanide, and thiocyanate ions. Different fabrication techniques, including PVC membrane, silicone grease, coated-wire, and pellet methods, were systematically investigated to identify the most effective electrode preparation strategy. The comparative

study revealed that the method of fabrication significantly influences the analytical performance of the electrodes, particularly with respect to sensitivity, selectivity, response time, reproducibility, stability, and operational lifetime. Among the investigated techniques, PVC membrane and pellet methods exhibited superior analytical characteristics, providing stable and reliable potentiometric responses over a wide concentration range.

The developed electrodes displayed nearly Nernstian behaviour, rapid response, satisfactory detection limits, and good selectivity towards their respective target anions. The effects of pH, temperature, ionic strength, and interfering ions were carefully evaluated, and the optimized experimental conditions ensured accurate and reproducible measurements. Thermodynamic investigations indicated that the electrode processes were stable and thermodynamically favourable, while statistical analysis confirmed the precision, reliability, and reproducibility of the experimental results. The low values of standard deviation and the high correlation coefficients obtained from calibration studies further validated the analytical performance of the fabricated electrodes.

The findings of this investigation demonstrate that silver-based inorganic anion selective indicator electrodes provide a simple, rapid, economical, and efficient alternative to conventional analytical techniques for the determination of inorganic anions. Their ease of fabrication, low operational cost, and excellent analytical performance make them highly suitable for routine potentiometric analysis, industrial quality control, environmental monitoring, water quality assessment, and laboratory research. Furthermore, the study provides valuable information for selecting appropriate electrode fabrication methods and optimizing operating conditions for improved electrochemical performance. Future research may focus on the development of nanostructured membrane materials, solid-contact electrode systems, and portable electrochemical sensors to further enhance the sensitivity, selectivity, durability, and practical applicability of silver-based anion selective indicator electrodes in modern analytical and industrial applications.

REFERENCES

1. Allen, P. L., & Hickling, A. (1957). The anodic oxidation of sulphide ions. *Transactions of the Faraday Society*, 53, 1626–1635.
2. Arrhenius, S. (1887). On the dissociation of substances dissolved in water. *Zeitschrift für Physikalische Chemie*, 1, 631–648.
3. Bakker, E., Bühlmann, P., & Pretsch, E. (1997). Carrier-based ion-selective electrodes and bulk optodes. *Chemical Reviews*, 97(8), 3083–3132.
4. Bard, A. J., & Faulkner, L. R. (2001). *Electrochemical Methods: Fundamentals and Applications* (2nd ed.). John Wiley & Sons.
5. Buck, R. P., Lindner, E., Kutner, W., & Inzelt, G. (2004). Recommendations for nomenclature of ion-selective electrodes. *Pure and Applied Chemistry*, 76(6), 1139–1160.
6. Clark, L. C., & Lyons, C. (1962). Electrode systems for continuous monitoring in cardiovascular surgery. *Annals of the New York Academy of Sciences*, 102(1), 29–45.
7. Galvani, L. (1791). *De viribus electricitatis in motu musculari commentarius*. Bologna.
8. Hulanicki, A., Glab, S., & Ingman, F. (1991). Chemical sensors: Definitions and classification. *Pure and Applied Chemistry*, 63(9), 1247–1250.
9. IUPAC. (2000). *Compendium of Analytical Nomenclature* (3rd ed.). Blackwell Science.
10. Kissinger, P. T., & Heineman, W. R. (1996). *Laboratory Techniques in Electroanalytical Chemistry* (2nd ed.). Marcel Dekker.

11. Koryta, J., Štulík, K., & Barek, J. (1993). *Electrochemistry*. John Wiley & Sons.
12. Nernst, W. (1888). Zur Kinetik der in Lösung befindlichen Körper. *Zeitschrift für Physikalische Chemie*, 2, 613–637.
13. Pungor, E. (1978). *Ion-Selective Electrodes*. CRC Press.
14. Ross, J. W. (1967). Solid-state and liquid membrane ion-selective electrodes. *Science*, 156(3780), 1378–1383.
15. Skoog, D. A., Holler, F. J., & Crouch, S. R. (2018). *Principles of Instrumental Analysis* (7th ed.). Cengage Learning.
16. Tanaka, T., Hirata, H., & co-workers. (1985). Phosphate and arsenate ion-selective electrodes based on insoluble lead compounds. *Fresenius' Zeitschrift für Analytische Chemie*, 320, 278–280.
17. Umezawa, Y., Bühlmann, P., Umezawa, K., Tohda, K., & Amemiya, S. (2000). Potentiometric selectivity coefficients of ion-selective electrodes. *Pure and Applied Chemistry*, 72(10), 1851–2082.
18. Wang, J. (2006). *Analytical Electrochemistry* (3rd ed.). John Wiley & Sons.
19. Zdrachek, E., & Bakker, E. (2019). Potentiometric sensing. *Analytical Chemistry*, 91(1), 2–26.
20. These references are appropriate for a research paper on silver-based inorganic anion selective indicator electrodes and include foundational as well as modern literature up to 2020.