

Article

A Nano-Sized Poly(aniline-co-thiophene) Based Solid-Contact Screen-Printed Electrode for Batch and Continuous Potentiometric Determination of Iodide

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Abstract

Two approaches are described for construction of a screen-printed planar electrode (SPE) for potentiometric determination of iodide ion. The first, involves preparation and application of iron(II) bathophenanthroline tetraiodoplumbate complex ($[\text{Fe}(\text{bphen})_3][\text{PbI}_4]$), as a sensitive and selective electroactive sensing material in a potentiometric electrode for iodide determination. The second is the use of a nano-sized poly(aniline-co-thiophene) (PANI-co-PT) as a solid-contact material in a planar miniaturized configuration. The SPE displays a Nernstian response for iodide ion with a calibration slope of -58.81 ± 0.69 mV/decade ($R^2 = 0.9998$) over a wide concentration range (9.17×10^{-7} – 6.94×10^{-3} mol/L), low detection limit (6.09×10^{-7} mol/L), rapid response time (5.0 ± 1.0 s) and long-life span (75 ± 3.0 d). The use of PANI-co-PT solid-contact layer significantly improves the ion-to-electron transduction, eliminates the formation of undesired thin water layer between the sensing membrane and the conducting substrate, prevents membrane delamination, enhances potential stability with a significantly reduced potential drift (8.32 ± 0.12 $\mu\text{V}/\text{min}$) and displays high redox capacitance (2.560 ± 0.040 mF). Water contact angle measurements confirm the increased hydrophobicity of the modified membrane electrode (from $44 \pm 0.8^\circ$ to $93 \pm 1.4^\circ$) and demonstrate the membrane ability to repel moisture and further stabilize the sensor response. The proposed sensor is successfully integrated into a flow injection analysis (FIA) system to enable real-time and continuous iodide monitoring with high precision, high sample throughput and applicability for quality control of pharmaceuticals and environmental monitoring.

Keywords: flow injection analysis (FIA); iodide sensing; method validation; poly(aniline-co-thiophene) (PANI-co-PT) solid-contact material; potentiometry; screen-printed electrode (SPE)



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1. Introduction

Iodine is an essential micronutrient that plays a crucial role in human health, primarily in the synthesis of thyroid hormones—thyroxine (T4) and triiodothyronine (T3) [1]. These hormones regulate metabolic processes, support neurological development, and influence cardiovascular, immune, and reproductive functions. However, iodine deficiency remains a significant global health concern, particularly in regions where soil and water contain insufficient levels of this element. This deficiency can lead to disorders such as goitre,

hypothyroidism, fluorosis, infertility, and cognitive impairments [2]. To mitigate these risks, salt and dairy product fortification have been widely implemented. Beyond its biological significance, iodine is extensively used in pharmaceuticals [3], antiseptics [4], radiographic contrast agents [5], and chemical synthesis [6]. Iodide tablets are also used against nuclear incidents by protecting the thyroid gland from exposure to radioactive iodine (e.g., a nuclear power plant accident) [3].

The determination of iodine and its ionic forms, particularly iodide (I^-), is crucial in various fields, including environmental monitoring, clinical diagnostics, pharmaceutical quality control, and food safety. Iodide occurs naturally and is also influenced by agricultural runoff and industrial discharge [7]. In biological fluids, iodide concentration is a key biomarker for thyroid function and iodine metabolism [8], necessitating precise measurement for medical diagnostics. Additionally, strict control of iodide levels in pharmaceutical formulations and nutritional supplements is crucial to ensure compliance with the safety and quality standards [9].

Various analytical techniques have been developed for iodide determination, including ion chromatography (IC) [10], reversed-phase high-performance liquid chromatography with ultraviolet detection (RP-HPLC/UV) [11], UV-Vis spectrophotometry [12], flow injection spectrophotometric analysis [13], atomic absorption spectroscopy [14], molecular absorption spectrometry (MAS) [15], electrophoresis [16], enhanced-multi-pass cavity/Raman scattering [17], inductively coupled plasma mass/spectrometry (ICP-MS) [18], and cyclic voltammetry [19]. While traditional methods such as ion chromatography (IC) offer high accuracy and sensitivity, these methods often require expensive instrumentation, complex sample preparation, and lengthy analysis times. Spectrophotometric methods, including catalytic and colorimetric assays, provide cost-effective alternatives but often suffer from limited selectivity, susceptibility to matrix interferences, and inapplicability for turbid or coloured test solutions. In contrast, potentiometric sensors are promising analytical tools due to their simplicity, rapid response, low detection limit, possible miniaturization, and field applications [20].

Potentiometric ion-selective electrodes (ISEs) have gained significant attention for iodide determination due to their ability to provide direct, real-time, and selective determination [21–31]. However, conventional ISEs typically incorporate an inner filling solution, which presents several limitations, including evaporation of the inner filling solution, external pressure fluctuations, and osmotic pressure variations caused by differences in ionic strength between the sample and the inner filling solution. These challenges hinder their application in portable point-of-need (PON) devices and continuous analysis. To overcome these limitations, coated-wire ion-selective electrodes have been developed to eliminate the need for an inner filling solution. However, this type of electrode suffers from the disadvantages of the small interfacial sensing area and the formation of an aqueous layer between the conductive substrate and the ion-sensing polymeric membrane. In addition, residual current passing through the ion-selective membrane can result in a signal drift and noise due to the formation of O_2/H_2O half-cell reactions [32].

Following these early developments, solid-contact ion-selective electrodes (SC-ISEs) have been introduced in the early 1970s, marking a major milestone in miniaturized potentiometry by replacing the internal filling solution with a solid electron conductor [33]. This conceptual transition enables simplified architectures, reduces device fragility, and laid the foundation for modern all-solid-state ISEs. Subsequent works explored various solid-contact configurations, confirming that SC-ISEs represent a mature platform rather than an emerging concept [34].

Over the past decades, three primary classes of solid-contact materials have been investigated: (i) carbon-based materials [35], (ii) conducting polymers [36], and (iii) hybrid

or composite materials [37]. Carbon-based materials such as porous graphite, carbon nanotubes, and ordered macroporous carbon offer high surface area and hydrophobicity, providing electrical double-layer capacitance and suppressing water layer formation; however, their susceptibility to spontaneous self-discharge and charge redistribution processes can compromise long-term potential stability [38]. In general, carbon-based solid-contact (SC) materials for ion-selective electrodes (ISEs) frequently exhibit limitations in long-term potential stability, reproducibility, and selectivity due to slow, unexpected redox processes, potential for water layer formation, and high surface adsorption, causing contamination. The development of three-dimensionally ordered macroporous (3DOM) carbon improves transduction capacitance and reduces potential drift, establishing carbon frameworks as robust solid-contact candidates [39].

Conducting polymers such as polyaniline (PANI), polythiophene (PT), and poly(3,4-ethylenedioxythiophene) (PEDOT) have also gained attention due to their redox capacitance, mixed ionic–electronic conductivity, and mechanical flexibility [40]. Despite their advantages, individual conducting polymers suffer from intrinsic drawbacks: PANI exhibits hydrophilicity and pH sensitivity that promote water layer formation, whereas PT derivatives may suffer from environmental instability and limited conductivity [41]. PEDOT-based contacts improve potential stability but often require dopants or surface modifications to maintain long-term performance [42].

To overcome limitations associated with single-component conducting polymers, hybrid materials and copolymerization strategies have emerged. In particular, copolymerizing aniline with thiophene yields a conjugated system that combines the high redox capacitance and conductivity of PANI with the enhanced hydrophobicity, π -electron delocalization, and environmental stability of PT, thereby improving transduction efficiency, suppressing water layer formation, and enhancing long-term potential stability relative to individual homopolymers. This synergistic behavior provides a rational basis for selecting poly(aniline-co-thiophene) (PANI-co-PT) as a solid-contact material for advanced SC-ISE platforms.

The present study presents a simple, sensitive, and selective solid-contact-based ion-selective electrode (SC-ISE) for the selective determination of iodide ions. The electrode is based on the use of iron(II) bathophenanthroline tetraiodoplumbate complex as a novel iodide-selective ion-pair exchanger and poly(aniline-co-thiophene) (PANI-co-PT) as a solid-contact transducer to improve charge transfer efficiency, minimize potential drift, and enhance long-term stability. Compared to previously reported iodide-selective SC-ISEs employing single-component conducting polymers or carbon materials, the present design introduces a copolymer-based solid-contact that offers superior hydrophobicity, redox buffering capability, and reduced water layer susceptibility, thereby addressing long-standing challenges associated with potential drift, signal noise, and limited operational lifetimes. The proposed sensor exhibits good selectivity for iodide ion over many common interfering ions, a wide linear response range, a low detection limit, a rapid response time, and a long-life span. Additionally, its successful operation under both static (batch) and hydrodynamic (flow injection) conditions demonstrates its suitability for real-time and continuous monitoring applications, supporting its relevance for modern point-of-need sensing.

2. Materials and Methods

2.1. Equipment

A Fourier-transform infrared spectrometer (FTIR) with attenuated total reflection (ATR) (Alpha II, Bruker ABCO, Billerica, MA, USA) was used. A field-emission scanning electron microscope (FESEM; QUANTA FEG 250, Thermo Fisher Scientific, Eindhoven,

The Netherlands) was employed to examine the surface morphology of nano poly(aniline-co-thiophene). Atomic force microscopy (AFM) measurements were performed using a Bruker Dimension Icon system (Bruker, Billerica, MA, USA), and the data were analyzed using NanoScope Analysis software (version 1.7, Bruker, Billerica, MA, USA). Elemental analysis (CHN(I)) was performed using a EUROVECTOR elemental analyzer (EUROVECTOR INSTRUMENT & SOFTWARE, Pavia, Italy) to quantitatively determine C, H, N, and I contents in the synthesized ion-pair. Atomic absorption spectrometry (AAS) measurements were carried out using a SAVANTA AA GPC instrument (GBC Scientific Equipment, Melbourne, Australia) for the quantitative determination of Fe and Pb. Constant-current chronopotentiometric (CP) measurements were conducted using a Metrohm potentiostat/galvanostat (Autolab Model 204) with NOVA 1.1 software (Metrohm Autolab B.V., Utrecht, The Netherlands). A combination Ross glass electrode (Orion 81-02, Thermo Fisher Scientific, Waltham, MA, USA) was used for pH measurements. All potentiometric measurements were performed at 25 ± 1 °C, using 0.01 mol/L sodium dihydrogen phosphate (NaH_2PO_4) as the standard background electrolyte and ionic strength adjuster, while additional comparative tests with other media (e.g., NaCl and oxalic acid) were also conducted. The potentiometric response was measured by the proposed iodide electrode and an Orion Research iodide electrode (Model 945300, Thermo Fisher Scientific, Waltham, MA, USA) in conjunction with an Orion Ag/AgCl single-junction reference electrode (Orion Model 9001, Thermo Fisher Scientific, Waltham, MA, USA) filled with 10% *m/v* KCl. Static and hydrodynamic potentiometric measurements were carried out using an EMF 16-channel potentiometer (Lawson Laboratories, Malvern, PA, USA; input impedance 10^{13} Ω), controlled by EMF Suite 1.03 software. Ion activities were calculated using the extended Debye–Hückel approximation [43], and liquid junction potential corrections were applied using the Henderson equation [44].

2.2. Materials and Reagents

All chemicals were of analytical grade and used without further purification. All solutions were prepared using deionized water (18.2 M Ω ·cm specific resistance) obtained from the Milli-Q PLUS reagent-grade water system (Millipore, Burlington, MA, USA).

High molecular weight poly(vinyl chloride) (PVC) powder, lead(II) nitrate ($\text{Pb}(\text{NO}_3)_2$), and bathophenanthroline (BPhen) ($\text{C}_{24}\text{H}_{16}\text{N}_2$) were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). Tetrahydrofuran (THF), dioctyl phthalate (DOP), tritolyl phosphate (TTP), and *o*-nitrophenyloctyl ether (*o*-NPOE) were obtained from Fluka (Ronkonkoma, NY, USA). Aniline ($\text{C}_6\text{H}_5\text{NH}_2$), thiophene ($\text{C}_4\text{H}_4\text{S}$), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), and potassium iodide (KI) were purchased from Sigma-Aldrich (St. Louis, MO, USA). A 0.1 mol/L stock solution of KI was freshly prepared and stored at 2 °C in brown bottles for further dilutions.

2.3. Synthesis of Iron(II) Bathophenanthroline Tetraiodoplumbate Complex

A 50 mg portion of bathophenanthroline (BPhen) was dissolved in 10 mL of a 60% (*v/v*) ethanol–water mixture. To this solution, 0.1 mL of 0.1 mol/L iron(II) sulfate (pH 4.0) was added. The mixture was heated with stirring for 5 min to maintain a clear solution, after which a few drops of ethyl alcohol were added to facilitate the formation of the $[\text{Fe}(\text{bathophen})_3]^{2+}$ complex. Tetraiodoplumbate complex $[\text{PbI}_4]^{2-}$ was prepared by mixing solutions of lead(II) nitrate and potassium iodide in a 1:4 molar ratio. This solution was added to the iron(II) bathophenanthroline complex, to form iron(II) bathophenanthroline tetraiodoplumbate complex (Scheme S1). The resulting reddish-brown precipitate was filtered off using Whatman No. 42 filter paper, washed with cold deionized water, dried for 24 h at room temperature, and ground into a fine powder for further use.

2.4. Synthesis of Poly(aniline-co-thiophene) Solid-Contact Material

Poly(aniline-co-thiophene) was synthesized via chemical polymerization. Freshly distilled aniline (5.48 mL, 0.06 mol) and thiophene (1.60 mL, 0.02 mol) were mixed with 200 mL of 1.0 mol/L HCl solution under constant stirring for 30 min. A 20 mL aliquot of 0.1 mol/L aqueous ammonium persulfate (APS) solution, as a polymerization initiator, was added dropwise to the mixture using a peristaltic pump at a rate of 0.5 mL/min, and the mixture was sonicated for 1 h. An intermediate dark green-coloured solution was observed, and the mixture was left to stand overnight. The resulting dark greenish-brown-coloured product of poly(aniline-co-thiophene) was separated from the reaction mixture using vacuum-assisted filtration, washed thoroughly with double-distilled water and methanol, and finally dried at 60 °C for 30 min. The dried product was ground into fine particles to obtain the final solid-contact material.

Chemical oxidative polymerization was selected because it enables batch preparation and straightforward drop-casting on disposable SPEs, while avoiding the use of an electrochemical cell setup required for electropolymerization. This batch-based approach was compatible with automated production workflows and facilitated scale-up.

2.5. Membrane Preparation and Sensor Construction

A poly(vinyl chloride) (PVC) membrane cocktail was prepared as described in our previous work [45]. A 2 mg portion (1.0 wt%) of iron(II) bathophenanthroline tetraiodoplate sensing ion-pair exchanger, 132 mg (66 wt%) *o*-nitrophenyloctyl ether as a plasticizer, and 66 mg (33 wt%) PVC was dissolved in 1.8 mL of tetrahydrofuran (THF). This composition corresponds to the final sensing membrane; additional membranes incorporating other plasticizers (DOP and TTP) with the same formulation were also prepared for comparative evaluation during the optimization studies. A 10 µL aliquot of the prepared membrane cocktail was drop-cast onto a screen-printed electrode (SPE) with a 3 mm-diameter circular carbon working electrode (model TE100, Zensor®, Taichung City, Taiwan). The coated SPE (unmodified) was left to dry at room temperature overnight. The electrode (SPWE) was conditioned by soaking in a 0.01 mol/L iodide aqueous solution overnight. For the modified SPWE, a 30 µL aliquot of a PANI-co-PT dispersion in THF (10 mg PANI-co-PT in 1.0 mL THF) was sonicated before use, drop-cast onto the bare screen-printed working electrode, and allowed to dry at room temperature overnight, ensuring homogeneous wet coverage over the 3 mm working area. Then, the PVC membrane cocktail was applied on the top of the PANI-co-PT layer, followed by conditioning in 0.01 mol/L iodide aqueous solution overnight.

2.6. Potentiometric Measurements

The screen-printed working electrode (SPWE), either unmodified or modified with PANI-co-PT as solid-contact material, was used in conjunction with an Orion Ag/AgCl single-junction reference electrode (Orion Model 9001) filled with 10% (*w/v*) KCl for potentiometric measurements. Calibrations were performed by transferring 0.5–1.0 mL aliquots of freshly prepared aqueous potassium iodide (KI) solutions with concentrations ranging from 1.0×10^{-6} to 1.0×10^{-1} mol/L to a 20 mL beaker containing 10 mL of 0.01 mol/L sodium dihydrogen phosphate (NaH_2PO_4) as an ionic strength adjuster. Potential readings were recorded at 25 °C after stabilization to ± 0.5 mV, and the electromotive force (EMF) was plotted against the logarithm of iodide concentrations. All potentiometric measurements were conducted using three independently prepared electrodes, and each concentration point was recorded in four replicate measurements to assess within-electrode precision and piece-to-piece reproducibility.

The effect of pH on the stability of the potentiometric response was evaluated over a pH range of 2–12 by adjusting the iodide test solution at various pH with NaOH or HNO₃ at constant iodide concentrations. The corresponding potentiometric responses were recorded against pH values. The selectivity coefficients (K_{I-J}^{pot}) of various interfering anions were determined using the separate solutions method (SSM) [46].

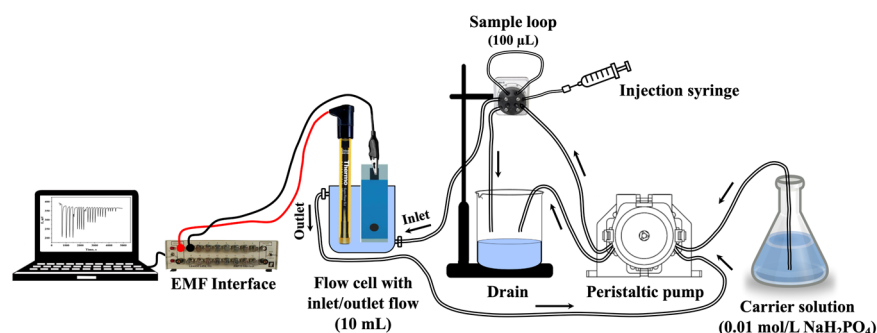
2.7. Analytical Applications

2.7.1. Potentiometric Titration of Metal Ions

A series of potentiometric titrations was conducted using the modified iodide screen-printed electrode (SPE) as an indicator sensor. Test solutions containing a single cation (Ag⁺ or Hg²⁺) and binary mixtures (Ag⁺ + Hg²⁺) were titrated with a standard iodide solution. The equivalence points at each inflection break were detected and correlated with the concentration of each metal ion. The stoichiometric relationship was determined as follows: 1.0 mol of iodide corresponds to 1.0 mol of Ag⁺ or 0.5 mol of Hg²⁺.

2.7.2. Flow Injection Setup for Potentiometric Iodide Determination

The flow injection setup consisted of a two-channel peristaltic pump, connected via polyethylene tubing (Tygon, 0.7 mm i.d., Saint-Gobain Performance Plastics, Akron, OH, USA) to an injection valve (Rheodyne, Model 7125, Rheodyne LLC, Rohnert Park, CA, USA) equipped with a 100 µL sample loop for injection [36]. A carrier solution (0.01 mol/L sodium dihydrogen phosphate (NaH₂PO₄)) was propelled by the peristaltic pump through polyethylene tubing (1.13 mm i.d.) with a total length of 30 cm, directing the flow from the injection valve to a custom-made compact flow cell. This flow cell was designed to house the iodide screen-printed electrode (SPE) and reference electrode, and to ensure controlled inlet and outlet flow, as illustrated in Scheme 1. The sample loop was filled and rotated, allowing the sample to enter the flow cell along with the carrier solution. A flow rate of 2.0 mL/min was maintained, and EMF signals were recorded using a high-impedance EMF interface (Lawson Laboratories, Malvern, PA, USA), controlled via EMF Suite 1.03 software.



Scheme 1. Schematic of the flow injection setup for potentiometric iodide monitoring, featuring a two-channel peristaltic pump, 100 µL injection valve, and a compact flow cell with iodide SPE and reference electrode.

The average peak height of four consecutive replicate runs was measured and compared with a calibration plot prepared under identical conditions.

3. Results

3.1. Characterization of the Iodide-Selective Ion-Pair Exchanger

Characterizations of the synthesized iron(II) bathophenanthroline tetraiodoplumbate [Fe(bphen)₃][PbI₄] ion-pair complex were carried out using elemental analysis and FTIR spectroscopy. The calculated elemental composition was: C 48.91%; H 2.71%; N 4.75%; Fe 3.16; Pb 11.73; I 28.75 compared to the experimentally found values: C 47.98%; H 2.67%;

N 4.45%; Fe 2.93%; I 27.95%; Pb 11.48%, thereby verifying the successful incorporation of these elements and confirming the successful formation of the intended ion-pair complex. The FTIR spectra of bathophenanthroline and its ion-pair complex were measured and shown in Figure S1. The FTIR spectra provided strong evidence for the successful formation of a 1:1 ion-pair complex. The spectrum of free bathophenanthroline exhibited a C=N stretching band at 1588.0 cm^{-1} and C=C stretching at 1493.3 cm^{-1} [47]. In the complex spectrum, these peaks were shifted to 1556.4 cm^{-1} and 1503.8 cm^{-1} , respectively, indicating coordination with Fe(II). In addition, the new band appeared in the 531.7 cm^{-1} region, corresponding to Fe-N vibrations, which was a further support of a metal-ligand interaction [48]. The intensities of these characteristic peaks decreased in the spectrum of the ion-pair complex, indicating an alteration in the ligand's electronic environment upon coordination. These spectral changes confirmed the successful formation of the ion-pair complex $[\text{Fe}(\text{C}_{24}\text{H}_{16}\text{N}_2)_3]^{2+}[\text{PbI}_4]^{2-}$.

3.2. Characterization of the Nano-Sized PANI-co-PT Solid Contact

3.2.1. FTIR Analysis

The successful copolymerization of aniline and thiophene to form poly(aniline-co-thiophene) (PANI-co-PT) was confirmed using Fourier-transform infrared spectroscopy (FTIR). Characteristic peaks corresponding to both monomeric units are shown in Figure S2. A broad band observed between 3454.2 cm^{-1} and 3249.9 cm^{-1} was attributed to N-H stretching of secondary amine groups in PANI. Peaks at 3055.1 cm^{-1} and 2950.6 cm^{-1} due to aromatic C-H stretching of thiophene and benzenoid rings were displayed [49]. The presence of distinct C=C stretching bands at 1620.4 cm^{-1} and 1519.8 cm^{-1} were characteristic of the quinoid and benzenoid structures, respectively. These peaks exhibited a noticeable red shift compared to pure PANI, suggesting an extended π -conjugation due to the presence of thiophene. Additionally, two peaks at 1378.6 cm^{-1} and 1297.2 cm^{-1} correspond to C-N stretching vibrations of the secondary amine group and C-N⁺ stretching in the polaron lattice, were due to the formation of the emeraldine and responsible for electrical conductivity. The oxidation of polythiophene units was supported by the peak that appears at 1142.4 cm^{-1} , assigned to C-S⁺ stretching.

Additional peaks provided further structural insights, with bands at 1194.2 cm^{-1} and 775.3 cm^{-1} corresponding to Q-NH⁺-B out-of-plane deformation and quinoid ring (Q-ring) deformation, respectively [50], reinforcing the successful formation of a conjugated system. The sharp peak at 714.6 cm^{-1} , attributed to C-S bending, confirmed the incorporation of polythiophene within the copolymer backbone [51]. The absence of monomeric functional groups further supported the formation of a well-structured, conjugated copolymer. The observed shifts in quinoid and benzenoid vibrations, alongside the presence of polythiophene oxidation markers, suggested that PANI-co-PT exhibited enhanced charge transport characteristics, making it a promising candidate for solid-contact potentiometric sensors.

3.2.2. FESEM and AFM Analysis

Field emission scanning electron microscopy (FESEM) of the synthesized poly(aniline-co-thiophene) (PANI-co-PT) copolymer confirms the successful formation of a well-integrated hybrid nanostructure. As shown in Figure 1a, the FESEM image exhibited a distinct combination of granular and fibrillar features, characteristic of polythiophene (PT) and polyaniline (PANI), respectively. The presence of nano-sized spherical granules, typical of PT, along with an interconnected fibrous network indicative of PANI, suggest the formation of a uniform polymeric framework with no significant phase separation [52]. The rough, porous surface observed in the FESEM image enhanced the copolymer surface area, which was expected to improve electrochemical performance and facilitate efficient

charge transfer. The absence of distinct phase boundaries was a further support for the formation of a true copolymer rather than a simple physical mixture of PANI and PT. This reinforced its potential as a solid-contact material in potentiometric sensor applications.

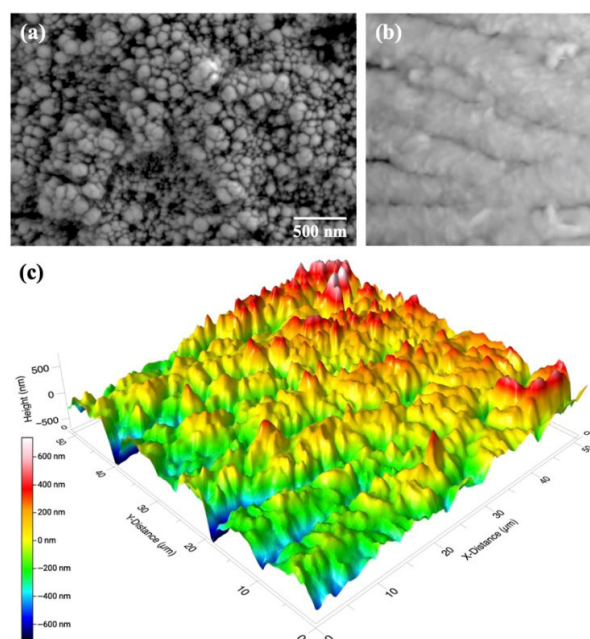


Figure 1. Surface morphology analysis of the synthesized nano-sized poly(aniline-co-thiophene) (PANI-co-PT) copolymer. (a) FESEM image. (b) AFM topographic image. (c) AFM 3D image. The cross-sectional area for AFM analysis was $50 \times 50 \mu\text{m}$.

Atomic force microscopy (AFM) was also used to evaluate the surface morphology of the copolymer after being drop-cast onto the surface of the screen-printed electrode (SPE) to assess its topographical uniformity and surface roughness. The AFM topographic image (Figure 1b) revealed a highly rough and porous surface with nano-sized cracks, which increased the overall surface area and improved the attachment of the PVC selective sensing membrane. This enhanced the adhesion of the copolymer and increased sensor sensitivity. In addition, the AFM 3D image (Figure 1c) showed an average thickness of 738.7 nm with an average roughness of 670.8 nm. These values were obtained by analyzing height profiles over a $50 \times 50 \mu\text{m}$ scan area using NanoScope Analysis software (Bruker), where the thickness corresponds to the mean vertical height of the deposited layer and the roughness represented the RMS (root-mean-square) surface roughness. The obtained AFM data further confirmed the porous and interconnected nanostructure of the copolymer, supporting its suitability as a solid-contact material for potentiometric sensor applications. The enhanced surface roughness observed in AFM analysis was beneficial for improving charge transfer kinetics and ensured a stable ion-to-electron transduction, which was essential for long-term sensor performance and reproducibility. It was clear that FESEM and AFM provided local morphological information, while the overall coating homogeneity on the SPE surface was ensured by the controlled deposition procedure described in Section 2.5.

3.3. Potentiometric Characteristics of the Iodide SPE

3.3.1. Potentiometric Response of Iodide Ions

Iron(II) bathophenanthroline tetraiodoplumbate, $[\text{Fe}(\text{bphen})_3][\text{PbI}_4]$ complex was examined as a novel iodide ion-pair exchanger in a PVC matrix membrane sensor. The PVC matrix membrane consisted of an optimum composition of 33 wt% PVC, 66 wt% *o*-NPOE (plasticizer), and 1.0 wt% iodide sensing complex. The 1.0 wt% ion-pair exchanger level was selected following preliminary optimization, where different loadings ranging

from 0.8 wt% to 2.0 wt% were evaluated and 1.0 wt% provided the most favourable potentiometric performance (Nernstian slope with rapid stabilization). Control tests using a PVC/o-NPOE membrane without the ion-pair exchanger showed no measurable iodide response, confirming that iodide recognition originates from the $[\text{Fe}(\text{bphen})_3][\text{PbI}_4]$ complex rather than the membrane matrix.

The potentiometric response characteristics of the proposed iodide sensor were evaluated before and after modification with poly(aniline-co-thiophene) (PANI-co-PT) as a solid-contact material. Measurements were performed using iodide solutions ranging from 1.0×10^{-6} to 1.0×10^{-1} mol/L in a 20 mL beaker containing 10 mL of 10^{-2} mol/L sodium dihydrogen phosphate (NaH_2PO_4) as an ionic strength adjuster, at pH 6.0. The unmodified sensor exhibited a linear response to I^- ions over the concentration range of 4.9×10^{-6} to 6.9×10^{-3} mol/L, with a detection limit of 1.1×10^{-6} mol/L (139.6 ppb). The response was a sub-Nernstian response with a calibration slope of -44.36 ± 0.93 mV/decade ($n = 6$, $R^2 = 0.9867$), and a response time of >60 s was observed. However, after modification with PANI-co-PT solid-contact material (Figure 2), the sensor exhibited an improved linear response (9.17×10^{-7} to 6.94×10^{-3} mol/L), a lower detection limit (6.09×10^{-7} mol/L, 77.3 ppb), a calibration slope of -58.81 ± 0.69 mV/decade ($n = 6$, $R^2 = 0.9998$), and a significantly faster response time (of 5 s). These results indicated that the modified SPE enhanced the potentiometric response, attributed to the fast and stable ion-to-electron transduction between the iodide ion-selective membrane, the solid-contact material, and the conducting substrate.

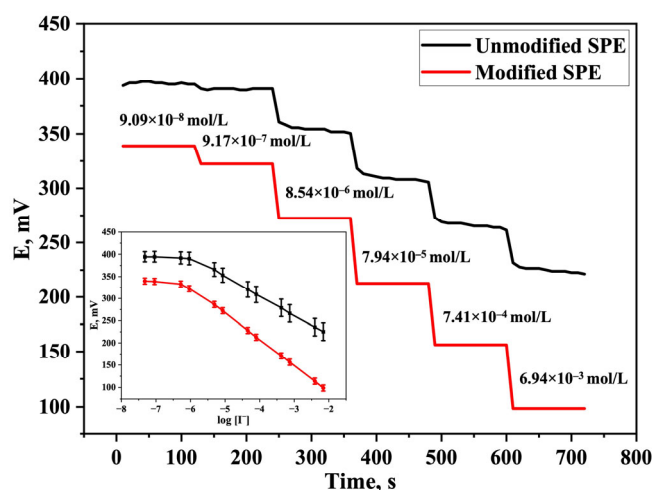


Figure 2. Potentiometric response of the iodide-selective SPE before and after modification with poly(aniline-co-thiophene) (PANI-co-PT) as a solid-contact material. (Inset: Calibration plots) (error bars represent the standard deviation from four replicate measurements performed on three independently prepared electrodes).

3.3.2. Effect of Solvent Mediators (Membrane Plasticizer) and pH

The polarity and dielectric constant of the membrane plasticizer significantly influenced the potentiometric performance of the modified iodide selective SPE. Three plasticizers with different dielectric constants were examined. Nitrophenyloctyl ether (*o*-NPOE, $\epsilon = 23.9$) exhibited the best performance, it provided the most stable response with the lowest iodide detection limit (6.09×10^{-7} mol/L) and a calibration slope of -58.81 ± 0.69 . Tritolyl phosphate (TTP, $\epsilon = 12$) exhibited a sub-Nernstian slope of -53.31 ± 0.24 mV/decade and a lower detection limit of 1.5×10^{-6} mol/L. Plasticizers with low dielectric constant, such as dioctyl phthalate (DOP, $\epsilon = 7$), did not show reasonable and stable potentiometric response and were unable to dissolve the iodide sensing material $[\text{Fe}(\text{bphen})_3][\text{PbI}_4]$ complex (molecular mass 1766.6).

The effect of pH on the sensor potential was also investigated by monitoring the potential variations over a pH range of 2–11 for 1.0×10^{-3} and 1.0×10^{-4} mol/L iodide solutions. As shown in Figure S3, the pH potential profiles indicated that the optimum operational pH range of the modified iodide selective SPE was 3.0–8.4. At pH values below 3, the high proton activity directly affects the interfacial potential and iodide is partially oxidized ($I^- \rightarrow I_2/I_3^-$), which decreases the free iodide activity in solution and destabilizes the electrode response. At pH values above 8.4, hydroxide ions interfere with the ion-exchange process and alter the membrane–solution equilibria, causing deviations from Nernstian behaviour. These effects define the restricted operational pH range (3.0–8.4). Additionally, calibration of the proposed electrode in different background solutions, including deionized water, 10^{-2} mol/L NaCl, 10^{-2} mol/L NaH_2PO_4 , and 10^{-2} mol/L oxalic acid indicated very little variation with no effect on the electrode performance.

3.3.3. Electrode Selectivity

The selectivity of the proposed iodide-selective screen-printed electrode (SPE) toward some common interfering anions was evaluated using the separate solutions method (SSM) [46]. The measurements were conducted under the optimized conditions, including the use of 1.0×10^{-2} mol/L NaH_2PO_4 as a background matrix, where the solutions contained either the primary or the interfering ion at the specified activity. The selectivity coefficient ($K_{I^-,j}^{pot}$) was determined using the equation:

$$\log K_{I^-,j}^{pot} = \frac{E_j - E_{I^-}}{S} + \left(1 - \frac{Z_{I^-}}{Z_j}\right) \log a_{I^-} \quad (1)$$

where S represents the calibration slope of the iodide electrode, Z_{I^-} and Z_j were the charges of the iodide ion and the interfering ion, respectively, and E_j and E_{I^-} were the corresponding potential readings of the interfering ion and iodide ion at the same concentration (1.0×10^{-3} mol/L).

The results obtained (Table 1) showed that both electrodes with and without solid-contact material followed the same general selectivity trend. However, the modified electrode with solid-contact material exhibited an improved selectivity. This enhancement was attributed to the ability of poly(aniline-co-thiophene) solid-contact (PANI-co-PT) to improve potentiometric characteristics by facilitating a faster and more stable ion-to-electron transduction mechanism. The solid-contact layer did not alter the intrinsic ion-exchange selectivity of the membrane, which was determined by the ion-pair exchanger and the membrane matrix; the apparent improvement arose from enhanced signal stability, reduced drift, and suppression of water layer effects, leading to lower noise and more reproducible potential readings under the applied conditions.

Table 1. Logarithmic selectivity coefficients ($\log K_{I^-,j}^{pot}$) for the unmodified and modified iodide selective SPEs.

Interfering Ion, j	$\log K_{I^-,j}^{pot}$	
	Unmodified Iodide Selective SPE	Modified Iodide Selective SPE
Br^-	−1.88	−2.57
SO_4^{2-}	−3.60	−3.81
BrO_3^-	−1.72	−2.41
Cl^-	−1.77	−2.60
F^-	−1.84	−2.84
NO_2^-	−1.67	−2.48
$Cr_2O_4^{2-}$	−3.71	−3.91

Table 1. Cont.

Interfering Ion, j	$\log K_{I-j}^{pot}$	
	Unmodified Iodide Selective SPE	Modified Iodide Selective SPE
HCO_3^-	−1.66	−2.44
IO_3^-	−1.18	−1.79
SCN^-	−0.98	−1.62
CN^-	−1.00	−1.56
NO_3^-	−1.77	−2.43

The selectivity order of most anions was consistent and in good agreement with the Hofmeister series [53]. The strongly chaotropic anions (SCN^- , CN^- , IO_3^- , NO_3^-) exhibited higher interference, whereas kosmotropic anions (SO_4^{2-} , $\text{Cr}_2\text{O}_4^{2-}$, F^-) showed lower interference, confirming an ion-exchange mechanism of response.

3.4. Impact of Solid-Contact Material in Potential Stability

The solid-contact material plays a crucial role in enhancing both the short- and long-term potential stability of many electrode systems [20]. The potential stability of sensors containing these materials was influenced by two primary factors. The first factor related to the formation of an aqueous thin layer between the conducting substrate and the PVC ion-selective membrane, which negatively affected the long-term potential stability, as well as reproducibility and repeatability. The second factor was the efficiency of the ion-to-electron transduction at the interface of the conducting substrate. This process can be hindered either by low double-layer capacitance or by a slow redox capacitance mechanism. Most carbon-based materials suffered from a self-discharge effect when a bias potential was applied, affecting long-term potential stability [54]. However, the use of a conducting polymer as described in the present study offered a more stable alternative, as they rely on redox capacitance, which remains unaffected by bias potential.

3.4.1. Short-Term Potential Stability

The short-term potential stability of the proposed iodide electrode was evaluated in the absence and presence of different amounts of PANI-co-PT as a solid-contact material using chronopotentiometry measurements. This assessment facilitated the optimization of the drop-casted PANI-co-PT layer beneath the PVC selective membrane while enabling the evaluation of the efficiency of the ion-to-electron transduction mechanism. The PANI-co-PT solid-contact material was dispersed in 1.0 mL of THF, and varying volumes of this solution (10, 20, 30, 40, and 50 μL) were drop-cast onto the screen-printed working electrode before applying the PVC sensing membrane cocktail.

Chronopotentiometry measurements (Figure 3) were conducted by applying a constant cathodic and anodic current of 1.0 μA for 10 s, repeated twice in a 0.1 mmol/L potassium iodide solution. Both the bulk membrane resistance (R) and redox capacitance (C_{red}) were determined using Equations (2) and (3) [55].

$$R = 2i / \Delta E \quad (2)$$

$$\Delta E / \Delta t = i / C_{red} \quad (3)$$

where ΔE represented the potential change, R was the bulk membrane resistance, i was the applied current, C_{red} denotes the redox capacitance, and Δt represented the time interval.

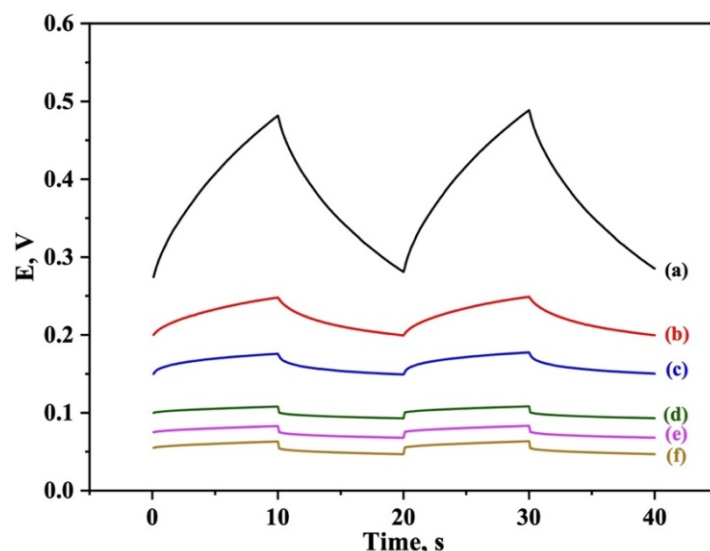


Figure 3. Chronopotentiometric response of (a) unmodified iodide screen-printed electrode (SPE) and (b–f) SPE modified with varying volumes (10, 20, 30, 40, and 50 μL) of drop-casted PANI-co-PT. Measurements were conducted in a 0.1 mmol/L potassium iodide solution under a constant cathodic and anodic current of 1.0 μA for 10 s, repeated twice. All measurements were repeated on independently prepared electrodes to verify reproducibility.

The results, summarized in Table S1, were reported as mean $\pm$ SD ($N = 3$), indicating a significant improvement in short-term potential stability upon modifying the iodide screen-printed electrode (SPE) with PANI-co-PT as a solid-contact material. This improvement was attributed to the high redox capacitance of the conducting copolymer, which enhances the ion-to-electron transduction mechanism. The superior redox capacitance observed can be attributed to the conjugated π -electron system of thiophene, which facilitated efficient electron delocalization and charge transfer, thereby improving the electrochemical performance. Increasing the amount of drop-casted PANI-co-PT from 10 to 30 μL caused an increase in the redox capacitance and a decrease in bulk membrane resistance. However, further increase in the amount to 40 μL resulted in a plateau, with no additional improvement in the redox capacitance or bulk membrane resistance. When the amount was increased to 50 μL , a marginal decrease in the redox capacitance and a slight increase in bulk membrane resistance were observed, likely due to the adsorption of the sensory material within the PVC selective membrane [45], which hindered the ion-to-electron transduction process. These findings confirm the efficiency of PANI-co-PT as a solid-contact material, with an optimum of 30 μL /electrode.

3.4.2. Long-Term Potential Stability

Water layer formation between the PVC selective membrane and the conducting substrate or solid-contact material was a critical issue that led to potential drift and long-term instability in electrode response. This thin aqueous layer facilitated uncontrolled ion exchange, redox reactions, and signal fluctuations over time, resulting in irreproducible responses and gradual response degradation. Therefore, preventing water layer formation through hydrophobic surface treatments was an essential step to ensure long-term sensor stability. To address this issue, the PANI-co-PT modification is investigated for its potential to eliminate the formation of the aqueous layer. The iodide screen-printed electrode (SPE) was immersed in a 0.1 mmol/L potassium iodide (KI) solution for 2 h before and after modification with PANI-co-PT. Subsequently, the electrode was transferred to a 0.01 mol/L sodium dihydrogen phosphate (NaH_2PO_4) solution for 2 h, followed by re-immersion in a 0.1 mmol/L potassium iodide (KI) solution for an additional 8 h (Figure 4).

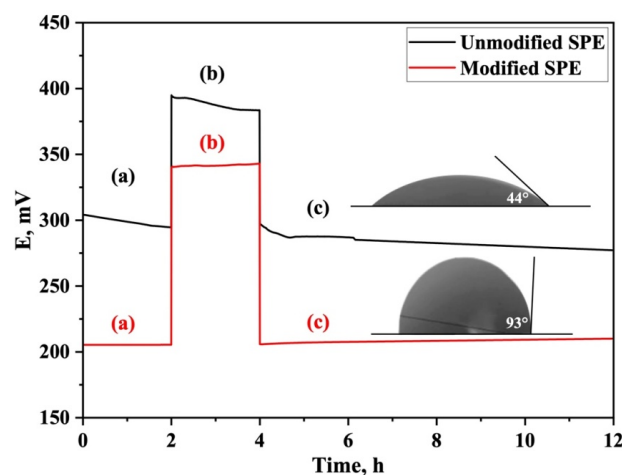


Figure 4. Water layer test of the iodide screen-printed electrode (SPE) before and after modification with the PANI-co-PT solid-contact layer in (a) 0.1 mmol/L KI, (b) 0.01 mol/L NaH_2PO_4 , and (c) 0.1 mmol/L KI. (Inset: water contact angle measurements). Measurements were performed on $N = 3$ independently prepared electrodes to confirm reproducibility.

The obtained results demonstrated the effectiveness of the PANI-co-PT solid-contact layer in eliminating the effect of a thin water layer and improving long-term potential stability. The presence of PANI-co-PT significantly reduced the potential drift from 84.11 ± 1.21 to 0.56 ± 0.01 $\mu\text{V}/\text{min}$ during the first 2 h, from 103.40 ± 1.55 to 15.96 ± 0.32 $\mu\text{V}/\text{min}$ in the next 2 h, and from 30.10 ± 0.45 to 8.32 ± 0.12 $\mu\text{V}/\text{min}$ over the final 8 h, confirming its ability to minimize water layer formation. In addition, water contact angle measurements, performed with 16 μL water droplet, showed an increase in the angle from $44^\circ \pm 0.8^\circ$ to $93^\circ \pm 1.4^\circ$ after modification with PANI-co-PT (Figure 4 inset). The significant enhancement of membrane hydrophobicity after application of the solid-contact layer, the significant improvement in the long-term potential stability, and the increase in water contact angle were attributed to the presence of thiophene in PANI-co-PT copolymer matrix, which provided lower surface energy than polyaniline and effectively repelled water molecules. Furthermore, thiophene contained a stronger π -electron conjugation system compared to polyaniline and thus reduced the interactions with water, enhancing the copolymer's hydrophobic nature. As a result, PANI-co-PT proved to be a highly effective material for solid-contact ion-selective electrodes.

3.5. Sensing Mechanism

The sensing mechanism of the proposed solid-contact iodide-selective SPE is based on an interfacial anion-exchange process at the solution/membrane boundary and redox-mediated ion-to-electron transduction at the solid-contact layer. The ion-selective responsive membrane (ISM) incorporates the lipophilic ion-pair $[\text{Fe}(\text{bphen})_3]^{2+}[\text{PbI}_4]^{2-}$, which supports selective partitioning and exchange of iodide ions from the aqueous test sample solution. It has been reported that lead poly-iodides possess unique anion-exchange properties, which are critical, fast at room temperature, and often undergoes reversible process [56]. Thus, the potentiometric response of $[\text{Fe}(\text{bphen})_3][\text{PbI}_4]$ based electrode to iodide ion is governed by an ion exchange process at the exposed surface of the electrode membrane, which creates an electrical double layer and establishes a phase boundary potential ($\Delta\Phi_1$) at the interface between the aqueous phase and the ISM. A potential difference proportional to the logarithm of iodide activity according to the Nernst equation is developed [20].

On the other hand, the use of a solid-contact conducting copolymer (PANI-co-PT) functions as a redox-capacitive transducer, converting ionic potential changes into electrical signals, and preventing water layer formation. During the ion-to-electron transduction process, PANI-

co-PT undergoes reversible redox transitions ($\text{PANI-co-PT}^+\text{Cl}^- + \text{e}^- \rightleftharpoons \text{PANI-co-PT}^0$), which provide electric charge compensation at the membrane/solid-contact interface. This mechanism does not rely on chloride exchange across the interface, and the membrane remains electrically neutral because anion uptake at the solution/membrane interface is balanced by redox charge adjustment within the solid-contact layer rather than by mobile counter-anions. This redox buffering ensures the stabilization of the interfacial potential ($\Delta\Phi_2$) between the ISM and the solid-contact layer, enabling a rapid and stable potentiometric response (Scheme S2).

The overall sensor performance is further enhanced by the hydrophobic nature of PANI-co-PT, which prevents moisture infiltration at the membrane-contact interface and significantly reduces long-term potential drift. The synergistic interaction between the ion-pair-based ISM, the redox-capacitive PANI-co-PT solid-contact layer, and the PVC matrix ensures a highly stable, selective, and sensitive potentiometric response for iodide determination across a broad concentration range.

3.6. Method Validation

The analytical performance of the PANI-co-PT modified iodide-selective SPE was validated by assessing trueness, accuracy, precision, repeatability, reproducibility, robustness, sensitivity, stability, and limit of detection (LOD). The validation protocol follows our previous report [57] and the results are summarized in Table 2.

Table 2. Method validation parameters of the PANI-co-PT modified iodide-selective SPE.

Parameter	Value $\pm$ SD
Slope, mV/decade *	-58.81 ± 0.69
Linear range, mol/L *	9.17×10^{-7} – 6.94×10^{-3}
Detection limit, mol/L *	$(6.09 \pm 0.12) \times 10^{-7}$
Correlation coefficient, R^2 *	0.9998
Working pH range, pH *	3.0–8.4
Response time, s *	5.0 ± 1.0
Standard electrode potential (E°), mV *	-34.47 ± 3.21
Redox capacitance (C_{red}), mF *	2.563 ± 0.074
Bulk membrane resistance (R), $k\Omega$ *	1.05 ± 0.12
Potential drift over 8 h, $\mu\text{V}/\text{min}$ *	8.32 ± 0.12
Precision, % ‡	0.5 ± 0.2
Accuracy (recovery), % ‡	96.7 ± 0.9
Trueness, % ‡	96.1 ± 0.6
Within-day reproducibility (CV_w), % ‡	0.35 ± 0.09
Between-days variability (CV_b), % ‡	0.51 ± 0.12
Relative standard deviation, % ‡	0.69 ± 0.08
Lifespan, days *	75 ± 3

* Values represent mean $\pm$ SD obtained from $N = 3$ independently prepared electrodes. ‡ Values represent mean $\pm$ SD obtained from n repeated measurements for analytical evaluation.

3.7. Analytical Application

3.7.1. Potentiometric Titration of Heavy Metal Ions

The modified iodide screen-printed electrode (SPE) was used as an indicator electrode for potentiometric titration of some metal ion solutions capable of forming metal iodide precipitates, such as Hg^{2+} , Ag^+ , Bi^{3+} , Pb^{2+} , and Cu^{2+} . A 10 mL aliquot of 1.0×10^{-3} mol/L Ag^+ and Hg^{2+} ions, both individually and in binary mixtures, was titrated with a standard iodide solution (1.0×10^{-3} mol/L) using the proposed electrode. The inflection breaks at the stoichiometric equivalent points were too large: 180 mV and 300 mV for silver and mercury ions, respectively. The equivalence points were obtained at 10.1 ± 0.2 mL ($101.0 \pm 2.0\%$

recovery) for Ag^+ and 4.9 ± 0.1 mL ($98.0 \pm 2.0\%$ recovery) for Hg^{2+} when titrating 10.0 mL of 1.0×10^{-3} mol/L solution with 1.0×10^{-3} mol/L iodide, confirming the expected 1:1 ($\text{Ag}^+:\text{I}^-$) and 1:2 ($\text{Hg}^{2+}:\text{I}^-$) stoichiometric ratios, respectively. For titration of binary mixture of Ag^+ and Hg^{2+} ions, the sequence of interaction with iodide (Hg^{2+} first followed by Ag^+) was observed without overlap; probably attributed to the significant difference in the solubility products of AgI ($K_{\text{sp}} = 8.52 \times 10^{-17}$) and HgI_2 ($K_{\text{sp}} = 2.9 \times 10^{-29}$) [58], which allowed distinct equivalence points resolution. Two successive equivalence points were identified at 4.9 ± 0.1 mL and 10.1 ± 0.2 mL ($101.0 \pm 2.0\%$ recovery) for Hg^{2+} and Ag^+ , respectively, confirming sequential precipitation behavior. These results demonstrated that the proposed electrode can function as a practical potentiometric indicator for argentometric titrations in both single-ion and binary systems.

3.7.2. Flow Injection Potentiometric Iodide Determination

Different concentrations of iodide ion, ranging from 1.0×10^{-6} to 1.0×10^{-2} mol/L, were injected through a 100 μL sample loop of the injection valve of the setup. A flow rate of 2.0 mL/min of 10^{-2} mol/L NaH_2PO_4 at pH 6.0 was used as a carrier solution. During flow-rate optimization (1–10 mL/min), higher flow rates resulted in broader and lower peaks due to increased dispersion, while lower flow rates produced sharper peaks but prolonged analysis time. Therefore, a flow rate of 2.0 mL/min was selected as a compromise that provides sharp and reproducible peaks with acceptable sample throughput under the FIA conditions. Each concentration was analyzed in four replicate injections to evaluate within-electrode precision, and the FIA measurements were repeated using three independently prepared electrodes to assess between-electrode reproducibility. The average peak height from each injected concentration was used to construct the calibration curves (Figure 5), which were used for determining iodide in unknown test solutions. Under optimized conditions, a linear response for iodide solutions of 10^{-2} – 10^{-6} mol/L ($R^2 = 0.9985$) was obtained, with a slope of -40.3 ± 0.9 mV/decade ($n = 4$ injections; $N = 3$ electrodes). This slope was lower than the steady-state batch value because FIA records transient peak potentials under continuous flow and does not allow the electrode to reach equilibrium. The FIA slope was consistent across replicate injections and independent electrodes, confirming stable performance and ruling out sensor degradation. The calibration curve was used for the determination of iodide in spiked tap water, dietary supplement, and mouthwash (Table 3). Results with average recoveries of $98.7 \pm 2.4\%$, $98.1 \pm 1.4\%$, and $98.0 \pm 1.9\%$ were obtained, respectively. These results compared favourably with results obtained using Orion iodide ion-selective electrodes.

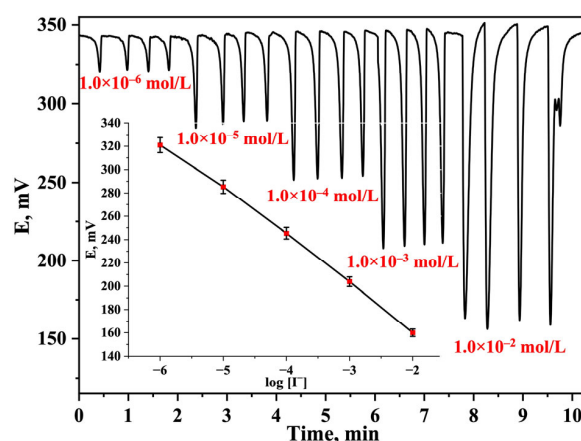


Figure 5. Flow injection potentiometric response of the modified iodide-selective SPE to different iodide concentrations. The inset shows the corresponding calibration curve of EMF (mV) vs. $\log [\text{I}^-]$, with error bars representing standard deviations from replicate measurements.

Table 3. Determination of iodide in spiked tap water, dietary supplement, and pharmaceutical samples using the flow injection potentiometric system and the proposed electrode.

Sample Type	Spiked, mg/mL	Proposed Iodide SPE		Orion Iodide Electrode	
		Found, mg/mL *	Recovery, %	Found, mg/mL *	Recovery, %
Tap water	0.05	0.049 ± 0.002	98.0 ± 4.0	0.047 ± 0.002	98.0 ± 4.0
	0.10	0.099 ± 0.002	99.0 ± 2.0	0.096 ± 0.003	99.0 ± 3.0
	1.00	0.991 ± 0.012	99.1 ± 1.2	0.982 ± 0.015	98.2 ± 1.5
Metabolics® Potassium Iodide Liquid Drops, dietary supplement, 0.076% (w/v) (Metabolics Ltd., East Sussex, UK)	0.0	0.762 ± 0.018	---	0.739 ± 0.021	---
	0.05	0.811 ± 0.017	98.0 ± 2.0	0.786 ± 0.024	94 ± 6.0
	0.10	0.859 ± 0.019	97.0 ± 1.0	0.832 ± 0.026	93 ± 5.0
	1.00	1.755 ± 0.030	99.3 ± 1.2	1.712 ± 0.035	97.3 ± 1.4
Betadine® Mouthwash & Gargle, 1% (w/v) (Mundipharma GmbH, Frankfurt am Main, Germany)	0.0	1.270 ± 0.025	---	1.220 ± 0.030	---
	0.05	1.319 ± 0.026	98.0 ± 2.0	1.268 ± 0.032	96.0 ± 4.0
	0.10	1.367 ± 0.028	97.0 ± 3.0	1.318 ± 0.034	98.0 ± 4.0
	1.00	2.260 ± 0.033	99.0 ± 0.8	2.170 ± 0.040	95.0 ± 1.0

* Average of 4 measurements (n = 4).

3.8. Advantages of the Proposed Iodide SPE

Many advantages were offered by using the proposed iodide electrode. The key advantage was the use of a novel iodide sensing ion-pair exchanger $[\text{Fe}(\text{bphen})_3][\text{PbI}_4]$, and the new solid-contact material (PANI-co-PT). Short response time (5.0 ± 1.0 s), long life span (>75 d), high stable readings (8.32 ± 0.12 $\mu\text{V}/\text{min}$ drift/8 h), miniaturized configuration (3 mm diameter), all-solid-state type without internal filling solution and ease of fabrication were displayed. These characteristics make the electrode amenable to use in static and hydrodynamic assay methods. In this work, $[\text{Fe}(\text{bphen})_3][\text{PbI}_4]$ was selected as the iodide ionophore because metal bathophenanthroline complexes exhibited excellent ion-exchange capacity with certain anions, freely soluble in membrane plasticizers, and possessed high hydrophobicity due to its high molecular mass (1766.6 g/mol).

A comparison of the potentiometric performance characteristics of the proposed electrode (SPE) with many of the previously reported electrodes is presented in Table 4. Conventional iodide liquid-based electrodes were bulky in size, required an inner filling solution and not easily miniaturized, whereas the coated-wire electrodes suffered from long response times (50–70 s), potential drift and short life span.

Table 4. Comparison of the main potentiometric characteristics of some previously reported Iodide-selective electrodes.

Sensory Material	Slope, mV/Decade	Linear Range, mol/L	Detection Limit, mol/L	pH Range	Response Time, s	Ref.
Triisobutylphosphine sulfide	−58.0	3×10^{-8} – 1×10^{-2}	2.0×10^{-9}	4.0–8.5	<60	[21]
Cobalt-salophen complex	−58.9	5×10^{-7} – 1×10^{-1}	3.0×10^{-7}	3.1–9.8	<15	[22]
Halogen bonding tripodal ionophore (XB1)	−51.9	1×10^{-6} – 1×10^{-1}	1.2×10^{-6}	--	--	[23]
Thiopyrilium ion derivative	−60.2	8.0×10^{-7} – 1.0×10^{-1}	2.0×10^{-7}	5.5–8.0	15	[26]
Cu(I) bathocuproine complex	−56.8	5.0×10^{-6} – 2.0×10^{-1}	1.0×10^{-6}	3.0–9.0	10	[27]
Iodide-miconazole ion-pair complex	−59.8	1.0×10^{-5} – 1.0×10^{-2}	7.0×10^{-6}	2.5–8.5	<20	[28]

Table 4. Cont.

Sensory Material	Slope, mV/Decade	Linear Range, mol/L	Detection Limit, mol/L	pH Range	Response Time, s	Ref.
Bis(2-mercaptobenzothiazolato) mercury(II)	−57.6	1×10^{-6} – 1×10^{-1}	4.0×10^{-7}	3.5–11.5	≤10	[24]
Bis(4-chlorothiophenolato) mercury(II)	−58.0		6.0×10^{-7}			
Phthalocyaninatotitanium(IV) oxide	−58.9	9.2×10^{-7} – 1.0×10^{-1}	8.5×10^{-7}	3.0–8.0	50–70 s ($>10^{-4}$ M), 2–3 min ($<10^{-4}$ M)	[25]
Phenyl mercury(II) (2-mercaptobezothiozolate)	−57.0	1.0×10^{-7} – 1.0×10^{-1}	8.0×10^{-8}	2.0–11.5	0.5	[29]
Bis[N(2-methyl-phenyl) 4-nitro-thiobenzamidato] mercury(II)	−58.9	1.0×10^{-6} – 1.0×10^{-1}	7.0×10^{-7}	3–11.5	5	[30]
Bis[N-phenyl 3,5-dinitro-thiobenzamidato] mercury(II)	−59.6	7.0×10^{-7} – 1.0×10^{-1}	3.0×10^{-7}			
Copper phthalocyanine	−56.0	5.0×10^{-6} – 1.0×10^{-1}	1.0×10^{-6}	3.0–8.0	<20	[31]
Cu-doped MgB ₂ (5% Cu)	−59.51 ± 0.4	4.53×10^{-7} – 6.18×10^{-3}	1.44×10^{-7}	3.8–6.0	≤6	[59]
iron(II) bathophenanthroline tetraiodoplumbate ion-pair complex	−58.8	9.2×10^{-7} – 6.9×10^{-3}	6.1×10^{-7}	3.0–8.4	5	This work

4. Conclusions

A simple, sensitive and selective solid-contact screen-printed electrode (SPE) modified with poly(aniline-co-thiophene) (PANI-co-PT) is developed to provide a highly sensitive, selective, and stable platform for potentiometric iodide determination. It incorporates an iron(II) bathophenanthroline tetraiodoplumbate complex as a sensing material dispersed in a plasticized PVC matrix membrane. The linear response range, calibration slope, detection limit and response time are 9.17×10^{-7} – 6.94×10^{-3} mol/L, -58.81 ± 0.69 mV/decade, 6.09×10^{-7} mol/L, and 5 s, respectively. The PANI-co-PT layer enhances ion-to-electron transduction, eliminates water layer formation, and ensures long-term potential stability, as validated by chronopotentiometric and water contact angle measurements. The sensor demonstrates good selectivity against many common interfering anions and offers a reliable and cost-effective tool for real-time iodide monitoring, with promising implications for clinical diagnostics, industrial quality control, and environmental surveillance.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym18040492/s1>, Scheme S1: Schematic diagram represents the process of synthesis of Iron(II) bathophenanthroline tetraiodoplumbate ion-pair complex; Figure S1: FTIR spectra of (a) free bathophenanthroline; and (b) the iron(II) bathophenanthroline tetraiodoplumbate $[\text{Fe}(\text{bphen})_3][\text{PbI}_4]$ ion-pair complex; Figure S2: FTIR spectrum of poly(aniline-co-thiophene) (PANI-co-PT); Figure S3: Effect of pH on the potentiometric response of the modified iodide-selective SPE, monitored over a pH range of 2–11 for 1.0×10^{-3} mol/L and 1.0×10^{-4} mol/L iodide concentration solutions; Scheme S2: Schematic diagram represents the sensing mechanism of the iodide-selective SPE modified with PANI-co-PT as a solid-contact material; Table S1: Bulk membrane resistance (R) and redox capacitance (C_{red}) of screen-printed electrodes (SPE) modified with varying volumes of drop-casted PANI-co-PT.

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Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author(s).

Conflicts of Interest: The authors declare no competing interests.

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