

A Solid-Contact Indium(III) Sensor based on a Thiosulfinate Ionophore Derived from Omeprazole

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A novel solid-contact indium(III)-selective sensor based on bis-(1*H*-benzimidazole-5-methoxy-2-[(4-methoxy-3,5-dimethyl-1-pyridinyl) 2-methyl]) thiosulfinate, known as an omeprazole dimer (OD) and a neutral ionophore, was constructed, and its performance characteristics were evaluated. The sensor was prepared by applying a membrane cocktail containing the ionophore to a graphite rod pre-coated with polyethylene dioxythiophene (PEDOT) conducting polymer as the ion-to-electron transducer. The membrane contained 3.6% OD, 2.3% oleic acid (OA) and 62% dioctyl phthalate (DOP) as the solvent mediator in PVC and produced a good potentiometric response to indium(III) ions with a Nernstian slope of 19.09 mV/decade. The constructed sensor possessed a linear concentration range from 3×10^{-7} to 1×10^{-2} M and a lower detection limit (LDL) of 1×10^{-7} M indium(III) over a pH range of 4.0-7.0. It also displayed a fast response time and good selectivity for indium(III) over several other ions. The sensor can be used for longer than three months without any considerable divergence in potential. The sensor was utilized for direct and flow injection potentiometric (FIP) determination of indium(III) in alloys. The parameters that control the flow injection method were optimized. Indium(III) was quantitatively recovered, and the results agreed with those obtained using atomic absorption spectrophotometry, as confirmed by the *f* and *t* values. The sensor was also utilized as an indicator electrode for the potentiometric titration of fluoride in the presence of chloride, bromide, iodide and thiocyanate ions using indium(III) nitrate as the titrant.

Key Words : Indium(III), Solid-contact sensor, Thiosulfinate, Omeprazole dimer, FIA

Introduction

Electrochemical potentiometric sensors are known to be excellent, low cost tools for the selective, sensitive and rapid determination of a vast variety of analytes for various applications.¹ Solid-contact ion sensors are especially interesting because they exhibit very low detection limits and are not limited by the presence of an inner reference solution found in conventional sensors.² Ionophore based ion-selective sensors have gained attention during the last decade because of their high selectivity,³ and sulfur-containing ionophores are extremely interesting.⁴ Thiosulfates are the salts of thiosulfonic acids that contain a -S-S(O) functional group. The biological activities of onion (*Allium cepa* L.), garlic (*Allium sativum* L.) and other edible *Allium* are attributed to thiosulfates,⁵ which are volatile sulfur compounds responsible for the pungency of these vegetables. The thiosulfates, or alkane(ene) thial-S-oxides, are formed by the alliinase enzyme present in the plant from their respective S-alk(en)yl cysteine sulfoxides. Whereas synthesized thiosulfates with electron-withdrawing substituents on the aromatic ring cannot be stably isolated from the reaction mixture, those with a releasing substituent in the *para*-position showed good stability.⁶ Omeprazole, a widespread proton pump inhibitor (PPI) containing sulfur, nitrogen and oxygen, was previously investigated as an ionophore for a gadolinium-selective electrode.⁷ However, omeprazole is not

a stable compound because it readily degrades in aqueous solution, especially at low pH values, and its maximum stability is at pH 11.^{8,9} Omeprazole's main acid-catalyzed decomposition product is sulfonamide, which reacts immediately with the sulfenic acid intermediate to form a dimer through the thiosulfinate functional group, as shown in Figure 1. The existence of the dimer compound was confirmed by a differential pulse polarographic study with 3.00×10^{-5} M omeprazole in a buffered solution at pH 4. A strong peak was assigned to the dimer hypothesized to be the major product from the acid decomposition of omeprazole.¹⁰ Therefore, we decided to investigate the stable thiosulfinate degradation product of omeprazole, *i.e.*, the omeprazole dimer¹¹ (Fig. 1), as a potential ionophore for heavy metal cations. Fortunately, it showed high selectivity for indium(III) ions. Indium is a rare element with a trivalent oxidation state and is extremely stable to atmospheric exposure. Indium is commonly used to make indium-tin oxide (ITO) for manufacturing liquid crystal displays (LCD's), accounting for 50% of its annual consumption.¹² Indium is also used to make photovoltaic devices, semi-conductors, high-speed transistors, specialized solders and metal alloys.¹³ Several methods are used to identify indium(III), including atomic absorption spectrometry,¹⁴ voltammetry,¹⁵ spectrophotometry¹⁶ and HPLC.¹⁷ However, only a few liquid or conventional ion selective electrodes (ISEs) have been described for indium(III),¹⁸⁻²⁰ and they exhibit similar drawbacks to

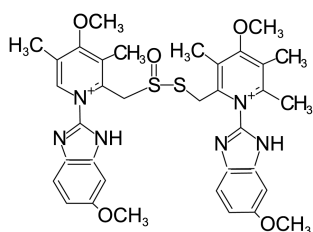


Figure 1. Bis(1*H*-benzimidazole, 5-methoxy-2-[(4-methoxy-3,5-dimethyl-1-pyridinyl)2-methyl]thiosulfinate (omeprazole dimer).

such types, such as difficult handling because of the presence of liquids or inner solutions. Additionally, some of the reported electrodes were not sensitive enough; their reported detection limits were approximately 10^{-5} M or higher and work in a narrow pH range. The present work describes the construction and evaluation of a novel sensitive all-solid sensor selective for indium(III) based on an omeprazole thiosulfinate ionophore. The developed sensor allows for easy manipulation, higher sensitivity and durability. In addition, the developed sensor was utilized for the flow injection potentiometric (FIP) determination of indium in alloys.

Experimental

All chemicals were analytical reagent grade unless otherwise stated and doubly distilled water was used throughout the experiments. Dioctyl phthalate (DOP), dibutyl phthalate (DBP), dibutyl sebacate (DBS), 2-nitrophenyl octyl ether (*o*-NPOE) and tetrahydrofuran (THF) were purchased from Aldrich. Potassium tetrakis(4-chlorophenyl)borate (KTPCLPB), oleic acid (OA), polyethylene dioxythiophene (PEDOT) and polyvinyl chloride (PVC) (high molecular weight) fine powder were purchased from Fluka. Omeprazole was obtained from European Egyptian Pharm. Ind., Alexandria, Egypt.

A 0.1 M indium(III) stock solution was prepared by dissolving an accurately weighed 2.2118 g sample of indium(III) chloride in 100 ml of distilled water. Working standards at 10^{-2} , 10^{-3} , 10^{-4} , 10^{-5} , 10^{-6} and 10^{-7} M concentrations were prepared by proper dilution of the stock solution. All potentiometric measurements were made at 25 ± 1 °C unless otherwise stated using a Metrohm pH/Ion meter (Model 692). A combined glass pH electrode (Metrohm 6.0202.100) was used for all pH measurements, and a Metrohm double junction Ag/AgCl reference electrode (Model 6.0726.100) containing 3 M potassium chloride in the outer and inner tubes was used as the reference electrode. UV/Visible spectrophotometric measurements were made using a Shimadzu 2040 spectrophotometer. The flow injection system consisted of an Ismatec model MCP peristaltic pump with Tygon R-3603 tubing with an i.d. of 0.25 mm, a homemade micro-flow cell with a 250- μ L volume and a PC-based EMF-16 high-resolution data logger (LAWSON) that was used to record and manipulate the output signals.

Preparation of the Thiosulfinate Ionophore. The contents of 20 Gastrazole capsules (containing approximately 400 mg of omeprazole) were dissolved in 50 mL of ethanol,

and the solution was filtered. The filtrate was slightly acidified and heated until the solvent was completely evaporated. The remaining red colored residue was recrystallized from ethanol and dried in air. Elemental analysis and UV-Vis, IR and mass spectroscopic analyses confirmed that the obtained product was the omeprazole dimer.¹⁰ Elemental analysis of the prepared compound confirmed the molecular formula: $C_{34}H_{38}O_5N_6S_2$ (674.835): element%: calculated and (found), C: 60.51 (60.46), H: 5.67 (5.57), N: 12.45 (12.40), S: 9.50 (9.48). IR (KBr) (ν_{max}/cm^{-1}): 3429, 2930, 1070, 1448, 601 and 450. MS peaks at m/z : 645, 461, 326, 281, 191, 147, 109, 97, 73 and 56. The UV spectrum in ethanol showed two peaks at 215 and 295 nm and a weak peak at 395 nm.

Construction of the Solid Contact Sensors. The sensitive membranes were prepared by mixing various amounts of the thiosulfinate ionophore with the proper amount of a plasticizer (DBS, DBP, NPOE or DOP), additive (OA or KpCIPB) and PVC and then dissolving it in THF. The prepared membranes contained ionophore ratios of 0.00, 1.84, 3.60, 5.32, 7.40 and 10.19%. The solid contact sensor was prepared using a spectroscopic-grade graphite rod (3 mm in diameter and 10 mm in length) with an insulated copper wire glued to one end with silver loaded epoxy resin. The working surface of the electrode was polished with a polishing cloth, rinsed with water and methanol and allowed to dry. A layer of the conducting polymer containing 0.5% poly(3,4-ethylene-dioxythiophene) doped with 0.8% poly(styrene-sulfonate) (PEDOT/PSS), an ion-to-electron transducer,²¹ was deposited on the graphite surface by dip-coating it several times and allowing it to air dry. The rods were then coated with ion-selective membranes with varying compositions. The newly constructed indium(III) sensors were calibrated by immersion in indium(III) chloride solutions with concentrations ranging from 10^{-7} to 10^{-2} M in pH 5.5 acetate buffer with continuous stirring. The potential was recorded after stabilization at ± 0.5 mV. Calibration graphs were constructed by plotting the recorded potential values versus $-\log$ [Indium(III)].

The influence of the test solution's pH on the potential response of the sensor was studied with 1.0×10^{-2} , 1.0×10^{-3} and 1.0×10^{-4} M indium(III) chloride solutions. The pH of each solution was adjusted by drop-wise addition of either HCl or NaOH, and the EMF of the electrode was recorded at each pH value after it stabilized.

Results and Discussion

The structure of the prepared thiosulfinate ionophore, *i.e.*, omeprazole dimer (OD), was confirmed by several analytical techniques including IR and MS. In the IR (KBr) spectrum of the prepared compound, the peaks at 601 and 450 cm^{-1} are characteristic of a disulfide group and an aryl disulfide group, respectively, which do not exist in the spectrum of omeprazole. The peak associated with the stretching of the sulfoxide (S=O) group in the omeprazole spectrum appeared at 1076 cm^{-1} and shifted to 1070 cm^{-1} in the prepared thiosulfinate compound's spectrum. In addition,

the N-H peak in the spectrum of omeprazole at 3050 cm^{-1} was observed at 3429 cm^{-1} in the spectrum of the prepared compound. The aromatic tertiary amine (C=N) peak, which occurred at 1660 cm^{-1} in the spectrum of omeprazole, was shifted to 1636 cm^{-1} in that of the prepared compound because of its rearrangement. The mass spectrum of omeprazole displayed a molecular ion peak at m/z 344 that corresponds to the total molecular weight of omeprazole.²² However, the mass spectrum of the prepared compound showed a molecular ion peak at m/z 645 that corresponds to the molecular weight of the thiosulfinate compound minus one methoxy group.

Membrane Composition. It is well known that not only the nature of the ionophore but also the membrane composition and the properties of the plasticizer and other ionic additives affect the sensitivity, selectivity and linearity of ISEs. Therefore, a careful study was performed to optimize the membrane composition. Membranes containing OD ionophore at 0.00%, 1.84%, 3.6%, 5.32%, 7.40% and 10.19% w/w concentration ratios were prepared, and their potentiometric response was evaluated using 10^{-7} to 10^{-2} M indium(III) chloride in acetate buffer solutions. The data in Table 1 summarizes that the performance of the sensor improved as the percentage of ionophore in the membrane increased up to 3.6%, above which the sensitivity decreased. The reason for this inflection may be attributed to saturation of the membrane or an increase in its homogeneity.²³ The membrane without ionophore (blank electrode) generated no potential response. Calibration graphs of the indium(III) sensors containing different percentages of the ionophore are presented in Figure 2. The plasticizer plays a vital role in sensor performance. It is responsible for the ionophore solvation and distribution in the membrane, thus controlling a sensor's sensitivity.²⁴ Several plasticizers including DOP, DBS, DBP and o-NPOE were evaluated as solvent mediators in the membrane. As shown in Table 1, DOP resulted in the

best sensor characteristics with a Nernstian slope and a wide linear working range. The presence of lipophilic anions in the cation-selective membrane electrodes diminishes the Ohmic resistance²⁵ and enhances their response behavior.²⁶ From the data in Table 1, it is obvious that the addition of 2.3% OA as an anionic lipophilic additive improved the slope and linear working range of the sensor and lowered its detection limit. However, increasing the amount of OA above this ratio did not beneficially influence the sensor's response; furthermore, the observed potential was unstable. The addition of other additives such as K-TpCIPB did not improve sensor performance.²⁷

The CGE constructed with a membrane containing 3.6% OD and 2.3% OA (No. 10) resulted in a quasi-Nernstian slope of 20.1 mV/decade with a linear concentration range of 1.3×10^{-6} to 1×10^{-2} M and a lower detection limit (LDL) of 1.0×10^{-6} M indium(III).

The optimized membrane composition, observed with sensor No. 10, was used to construct electrodes with conventional and all-solid contact types (sensor No. 15). The characteristic potentiometric performance of these two types

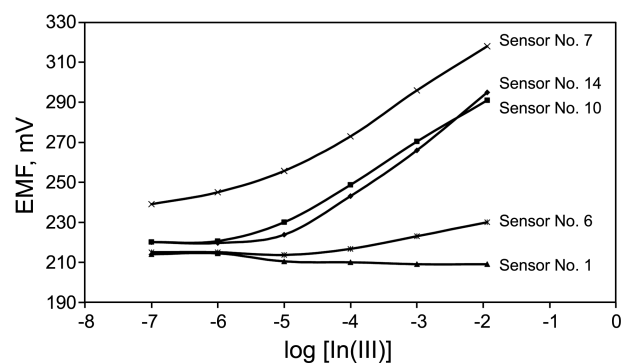


Figure 2. Effect of membrane composition on the potentiometric response of the coated graphite indium(III) sensors.

Table 1. Effect of various membrane compositions on the performance characteristics of the indium(III) sensor

No.	PVC%	OD%	P%	OA%	KpCIPB%	S	L.D.L	Linear range
1	35.56	0	64.4	—	—	—	—	—
2	34.99	1.84	63.1	—	—	12.0	3.9×10^{-6}	$6.3 \times 10^{-6} - 1 \times 10^{-2}$
3	34.35	3.60	62.0	—	—	19.9	2.1×10^{-6}	$3.9 \times 10^{-6} - 1 \times 10^{-2}$
4	33.74	5.32	60.9	—	—	28.0	4.1×10^{-6}	$6.4 \times 10^{-6} - 1 \times 10^{-2}$
5	32.87	7.40	59.3	—	—	23.0	6.3×10^{-6}	$6.3 \times 10^{-6} - 1 \times 10^{-2}$
6	32.04	10.19	57.8	—	—	0.80	—	—
7	33.97	3.60	62.5 ^a	—	—	26.9	6.3×10^{-6}	$8.1 \times 10^{-6} - 3 \times 10^{-3}$
8	35.30	3.70	61.0 ^b	—	—	24.9	7.9×10^{-6}	$1.0 \times 10^{-5} - 1 \times 10^{-2}$
9	37.30	3.70	59.0 ^c	—	—	11.5	5.0×10^{-6}	$6.5 \times 10^{-6} - 1 \times 10^{-22}$
10	32.10	3.60	62.0	2.3	—	20.1	1.0×10^{-6}	$1.3 \times 10^{-6} - 1 \times 10^{-2}$
11	29.10	3.60	60.0	7.3	—	30.6	1.0×10^{-5}	$1.0 \times 10^{-5} - 1 \times 10^{-2}$
12	33.80	3.70	62.0	—	0.5	20.0	9.0×10^{-6}	$1.0 \times 10^{-5} - 1 \times 10^{-2}$
13	34.30	3.60	61.1	—	1.0	23.0	8.0×10^{-6}	$1.1 \times 10^{-5} - 1 \times 10^{-2}$
14	33.00	3.60	62.0	—	1.5	25.0	9.0×10^{-6}	$1.0 \times 10^{-5} - 1 \times 10^{-2}$
15^a	32.10	3.60	62.0	2.3	—	19.09	1.0×10^{-7}	$3.0 \times 10^{-7} - 1 \times 10^{-2}$

^aAll sensors are coated graphite except sensor No. 15 which is a solid contact sensor. P = plasticizer, DOP except for ^aDBP. ^bDBS and ^cNPOE. L.D.L. = lower detection limit

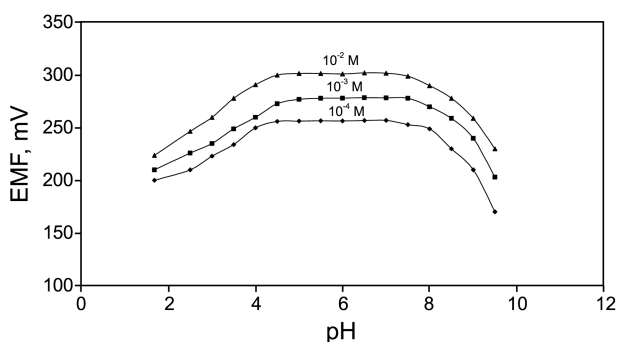
Table 2. The performance characteristics of all-solid state and CG indium(III) selective electrodes based on the OD carrier with optimized composition

Properties	Values/range	
Type of electrode:	All-solid contact	Coated-graphite
pH range	4.5-7.5	4.5-7.5
Linear range (In ³⁺ , M)	1 × 10 ⁻² - 3 × 10 ⁻⁷	1 × 10 ⁻² - 1.3 × 10 ⁻⁶
Slope, mV/conc. decade	19.09	20.1
Intercept, mV	342	345
Detection limit ± S.D., M	1 × 10 ⁻⁷	1.0 × 10 ⁻⁶
Response time, s	10-20	15-25
Life time, days	> 90 days	~60 days

of indium(III) sensors, as evaluated using 10⁻⁷ to 10⁻² M indium(III) chloride in pH 5.4 acetate buffer according to IUPAC recommendations,²⁸ are provided in Table 2.

The data in Table 2 show that the sensor with a solid contact configuration had the best performance with a Nernstian slope of 19.09 mV/decade and a linear range of 3 × 10⁻⁷ to 1 × 10⁻² M and a LDL of 1 × 10⁻⁷ M for indium(III). This result was expected because PEDOT, one of the most stable conducting polymers currently available, was used. It is particularly suitable as a solid contact material for this type of sensor due to its low sensitivity to O₂ and CO₂.²⁹ The cross-linked conducting polymer films are water-soluble and hence stabilize the standard potential of the sensors.³⁰ The effect of pH on the performance of the indium(III) sensor was investigated by measuring the sensor's response to 1 × 10⁻⁴, 1 × 10⁻³ and 1 × 10⁻² M indium(III) chloride solutions at pH 1-10; the pH was adjusted with HCl and/or NaOH. The sensor showed a stable response over the pH range 4.5-7.5, as shown in Figure 3, and after investigating the influence of different buffer solutions, the sensor demonstrated optimum performance in acetate buffer at a pH of 5.5. In this buffer solution, the coated graphite electrode, No. 10, showed a fast response time of 15 s. The repeatability (*n* = 5) and reproducibility of the calibration parameters of the proposed indium(III) sensor were studied by successively calibrating with the same membrane and the same ionic media on the same day and on different days (*n* = 10).

The repeatability and reproducibility of the sensor were found to be within ± 1.0 mV and ± 1.7 mV, respectively. The

**Figure 3.** Effect of pH on the indium(III) ISE (No. 10) using 10⁻² M, 10⁻³ M and 10⁻⁴ M indium(III) concentrations.**Table 3.** Selectivity coefficients ($K_{In,B}^{pot-SSM}$) of diverse ions relative to In(III) for CG and solid contact (with PEDOT) sensors measured using SSM

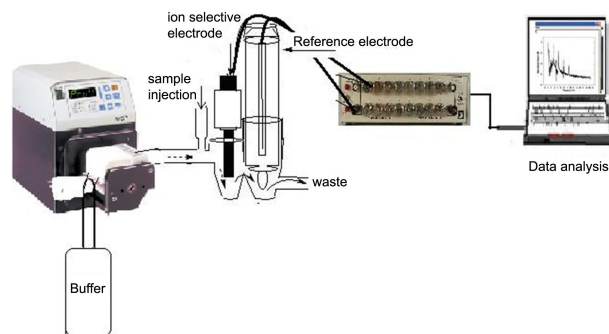
Ion	CG	Solid-contact	Ion	CG	Solid-contact
Cs ⁺	2.9 × 10 ⁻³	9.8 × 10 ⁻⁴	Fe ²⁺	2.3 × 10 ⁻⁴	1.9 × 10 ⁻⁴
Rb ⁺	8.4 × 10 ⁻⁴	1.1 × 10 ⁻⁴	Sn ²⁺	8.6 × 10 ⁻³	2.2 × 10 ⁻³
Ag ⁺	1.2 × 10 ⁻²	9.8 × 10 ⁻³	Cu ²⁺	1.2 × 10 ⁻³	1.0 × 10 ⁻⁴
I ⁻	9.5 × 10 ⁻⁴	2.0 × 10 ⁻⁴	Mn ²⁺	9.5 × 10 ⁻³	3.0 × 10 ⁻⁴
Br ⁻	1.1 × 10 ⁻⁴	1.9 × 10 ⁻⁴	Ni ²⁺	1.2 × 10 ⁻⁴	2.3 × 10 ⁻⁵
F ⁻	1.0 × 10 ⁻⁴	3.1 × 10 ⁻⁴	Fe ³⁺	1.5 × 10 ⁻²	1.0 × 10 ⁻²
SCN ⁻	9.1 × 10 ⁻⁵	1 × 10 ⁻⁴	Al ³⁺	1.1 × 10 ⁻²	2.0 × 10 ⁻³
Pb ²⁺	5.3 × 10 ⁻⁴	2.9 × 10 ⁻⁴	Ce ³⁺	6.3 × 10 ⁻³	3.9 × 10 ⁻⁵
Cd ²⁺	1.4 × 10 ⁻³	4.0 × 10 ⁻⁴	Ga ³⁺	6.3 × 10 ⁻²	3.6 × 10 ⁻³
V ²⁺	1.5 × 10 ⁻²	7.0 × 10 ⁻³	Eu ³⁺	2.0 × 10 ⁻³	2.9 × 10 ⁻⁵

potentiometric selectivity coefficient of an ion selective sensor is a measure of the electrode's ability to respond primarily to the analyte ion in the presence of interfering ions with the same charge. The effect of diverse ions on the response of the proposed indium(III) sensors was evaluated according to the IUPAC-recommended separate solution method (SSM),³¹ in which the potential of a 10⁻² M indium(III) chloride solution was measured, and then the potential of a 10⁻² M solution of a diverse ion was measured, and the following equation was applied:

$$\log K_{In,B}^{pot} = \frac{E_B - E_{In}}{S} - \left[\frac{1 - Z_{In}}{Z_B} \right] \log [In]$$

where $K_{In,B}^{pot}$ is the potentiometric selectivity coefficient, *S* is the slope of the calibration plot, [In] is the activity of the In(III) ion, and *Z*_{In} and *Z*_B are the charges of indium(III) and the interfering anions, respectively. Table 3 shows the selectivity coefficients of several diverse ions for both CGE and all-solid state electrodes using the SSM. Both sensors demonstrated the ability to discriminate indium(III) from the cations studied. The selectivity coefficients for V(II), Fe(III), Al(III) and Ga(III) were considerably improved using the all-solid state sensor, which is considered to be highly selective, compared to previously reported electrodes.

Flow Injection Analysis (FIA). FIA of indium(III) was

**Figure 4.** Schematic diagram of the flow injection manifold (a) and homemade mini flow-cell for the coated graphite electrode, No. 15 (b).

performed on the proposed solid contact sensor using a homemade flow-cell with pH 5.5 acetate buffer as a carrier. A schematic diagram of the flow injection manifold is shown in Figure 4.

The parameters of the FIA method were optimized to obtain the best signal sensitivity and sampling rate under low dispersion conditions. The geometry of the flow-cell limited the sample dispersion, which allowed for optimum sensitivity and fast response of the sensor. The effects of sample injection volume (100-500 μL) and carrier flow rate (15-40 mL/min) were examined. A high sample volume yielded high peak heights, long residence times and low sample throughput. With a constant injection volume, the residence time of the sample was inversely proportional to the flow rate. A sample volume of 500 μL and a flow rate of 30 mL/min were found to produce optimum results. The optimum conditions had a residence time of $T = 12$ s (T , the time span from injection until the appearance of the maximum signal), a travel time of $t = 3$ s (t , the time elapsed from injection to the start of the signal), a return time of $T' = 27$ s (T' , the time span between the appearance of the maximum signal and the return to baseline) and a baseline-to-baseline time of $\Delta T = 39$ s (ΔT or peak width, the interval between the start of the signal and its return to the baseline). These results proved that the proposed sensor possesses a very fast response toward indium(III) ions and can be rapidly washed, allowing for a sampling rate of at least 60 samples per hour. At flow rates higher than 30 mL/min, the response deteriorates rapidly. The calibration of the proposed indium(III) solid contact sensor in the concentration range of 10^{-6} - 10^{-2} M is shown in Figure 5.

Analytical Application. The indium(III) sensor was utilized as a detector for batch and flow experiments to determine the indium(III) ion concentration. The determination of indium(III) in binary and ternary mixtures with several of its alloying metals was achieved.

The sensor was successfully used for the determination of In(III) in In-Cd, In-Ga, In-Ag, In-Pb, In-Au, In-Sn and In-Cu

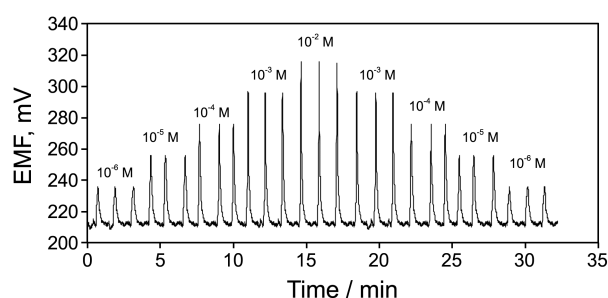


Figure 5. Calibration of indium(III) solid contact sensor (No. 15) using a sample volume of 500 μL and a flow rate of 30 mL/min.

binary and ternary mixtures, and the results are summarized in Table 4. The following linear equation from the calibration line of the indium(III) sensor was used to calculate the indium(III) concentration in the sample solution:

$$E = 342 + 19.09 \times \log [a_{\text{In}}]$$

The data showed a very good agreement with the nominal values given for each mixture. The sensor demonstrated practical utility compared to the atomic absorption spectrophotometric (AAS) method because of its increased accuracy, response and output. The F and t values from the F -test and Student's t -test are shown in Table 4 for the proposed potentiometric method and a standard AAS method; compared to their theoretical values of $F = 6.39$ and $t = 2.31$, there is no significant difference between the mean values and the precision of the two methods at a 95% confidence level. Because the means were statistically alike, the ratio of the variances for $N-1 = 4$ degrees of freedom (one-tailed F -test, $P = 0.05$) yielded F values less than the critical value of F , *i.e.*, $F = 6.388$.

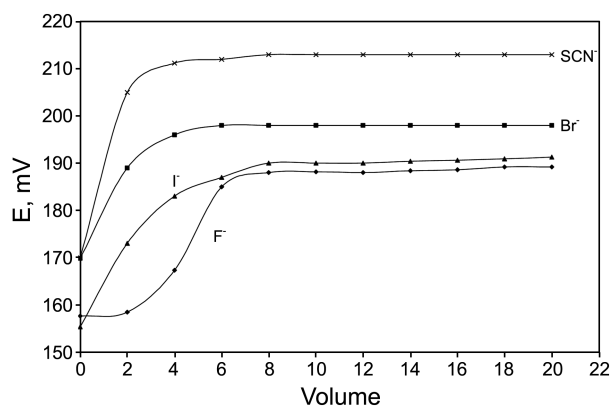
Therefore, the proposed potentiometric and AAS methods had similar precisions. The FIA method had a better slope, linear range and lower detection limits, and using the proposed miniaturized solid contact sensor and a homemade flow-cell under optimum experimental conditions, it was

Table 4. Determination of indium(III) in synthetic mixtures of several alloys using direct potentiometry (DP), flow injection potentiometry (FIP) and AAS, including the estimations of the F -test and T -test factors

Alloy No*	Composition, M, %	FIP			DP			AAS			F-test	T-test
		In ($\mu\text{g/mL}$)			In ($\mu\text{g/mL}$)			In ($\mu\text{g/mL}$)				
		added	found	R% \pm SD	added	found	R% \pm SD	added	found	R% \pm SD		
3026	In,75 - Cd,25	26.79	27.21	101.6 \pm 0.5	5.94	6.05	101.0 \pm 0.4	8.56	9.10	106.0 \pm 0.4	0.59	0.01
3006	In,97 - Ag,3	26.79	26.80	100.0 \pm 0.5	6.79	6.80	101.0 \pm 0.5	7.99	8.02	103.0 \pm 0.2	0.54	0.05
3002	In,80 - Pb,20	26.79	27.66	103.5 \pm 0.4	6.31	6.41	103.0 \pm 0.3	9.13	9.15	102.0 \pm 0.2	0.24	0.02
3008	In,70 - Pb,30	26.79	27.65	102.94 \pm 0.3	5.59	5.54	98.0 \pm 0.6	7.99	7.97	99.0 \pm 0.4	0.43	0.02
3004	In,60 - Pb,40	26.79	27.21	101.6 \pm 0.5	4.80	4.90	102.0 \pm 0.4	6.85	7.25	104.0 \pm 0.4	0.22	0.02
3005	In,50 - Pb,50	26.79	26.95	100.6 \pm 0.4	3.99	4.20	105.0 \pm 0.4	5.70	5.72	103.0 \pm 0.4	0.93	0.06
1052	In,40 - Pb,60	26.79	26.64	99.4 \pm 0.3	3.20	3.30	103.0 \pm 0.2	4.56	4.90	107.0 \pm 1.4	0.55	0.03
1038	In,19 - Pb,80	26.79	26.35	98.4 \pm 0.3	1.60	1.63	101.0 \pm 0.4	2.28	2.39	105.0 \pm 0.6	0.52	0.19
1011	In,20 - Au,80	26.79	26.69	99.6 \pm 0.3	1.598	1.60	100.6 \pm 0.4	2.28	2.26	98.0 \pm 0.4	0.89	0.11
1630	In,15 - Cu,24 - Ag,61	26.79	26.80	100.0 \pm 0.5	1.198	1.148	101.0 \pm 0.5	2.28	2.25	99.0 \pm 0.3	0.80	0.02
-	In,50 - Sn,50	26.79	28.06	102.8 \pm 0.5	3.99	4.22	105.0 \pm 0.4	5.70	6.20	109.0 \pm 0.9	0.61	0.01

Table 5. Stability constants of indium(III) complexes with halide ions³²

Halide	log K_1	log K_2	log K_3
F ⁻	3.7	2.66	2.3
Cl ⁻	2.47	0.64	0.83
Br ⁻	2.01	1.09	0.18
I ⁻	1.64	0.91	-0.08
SCN ⁻	2.53	1.35	0.92

**Figure 6.** Potentiometric titration curves for titration of 15 mL of 1×10^{-3} M fluoride, bromide, iodide and thiocyanate ions with a 1×10^{-3} M indium(III) chloride solution.

possible to determine indium(III) within different alloys. The analytical feasibility of the sensor was also investigated by using it as an indicator electrode for a potentiometric titration. When 10 mL of 1×10^{-3} M In(III) solution was titrated against a 1×10^{-3} M EDTA solution buffered at pH 5.5, a decrease of approximately 20 mV was observed, indicating that indium(III) can be accurately determined using the proposed sensor. In addition, indium(III) is known to form a stable fluoride complex with a high stability constant³² compared to the relatively low stability constants of the indium(III) chloride, bromide, iodide and thiocyanate complexes, as shown in Table 5.

The importance of determining the fluoride concentration in various matrices led to the investigation of using the proposed indium(III) sensor as the indicator electrode in its potentiometric titration. Therefore, 20.0 mL solutions of 1.0×10^{-3} M fluoride, bromide, iodide or thiocyanate were titrated with a 1.0×10^{-3} M In(III) solution at pH 5.5. The titration curves shown in Figure 6 indicate that indium(III) reacts only with the fluoride ion, and there is no inflection point in the titration plots of iodide, bromide and thiocyanate. The inflection point for the titration of the fluoride ion appears at 6.67 mL, indicating that the stoichiometric ratio of the reaction between the In(III) ions and F⁻ is 1:3. The fluoride concentration in the presence of other halides can be easily and accurately determined from the sharp inflection point of the titration curve using the proposed electrode.

Conclusion

The thiosulfinate ionophore used in the construction of the proposed sensor showed a selective response towards the trivalent indium(III) ion. The solid contact sensor allowed for a lower detection limit of 1.0×10^{-7} M for indium(III) compared to 1.0×10^{-6} M as seen with the coated graphite sensor. The solid contact sensor was also more accurate and possessed a faster response and longer durability. By exploiting the excellent characteristics displayed by the proposed sensor with FIA, a faster, more accurate and more practical method for identifying indium(III) in alloys was demonstrated.

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