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Research Article

Potentiometric Monitoring of Iodide Ions Using a Highly Selective Iodide Sensor Based on AgI-Cu_2S-Multi Walled Carbon Nanotube Material

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Abstract

In this work, a new iodide selective sensor based on a silver(I) iodide (AgI) – copper(I) sulphide (Cu_2S) –multi walled carbon nanotube (MWCNT) – Graphite (G) -Paraffin oil (PO) composite material was described for highly selective potentiometric determination of iodide ions. To obtain the best potentiometric performance characteristics of the sensor, the sensor components was optimized and the sensor was formed by properly pressing of the optimized sensor components. The experimental results were showed that the most appropriate potentiometric response was achieved with the sensor materials containing a compositions of G:MWCNT:AgI:Cu_2S:PO in the ratio 50:5:20:5:20 (% w/w). The developed sensor display a wide linear working range (1.0×10^{-5}-1.0×10^{-1} $molL^{-1}$) for iodide ions. In this linear working range, the Nernstian slope of the sensor was 51.5±1.0 mV and the correlation coefficient (R^2) was determined as 0.9991. The sensor was of a very low response time (5 s). The repeatability of the sensor potential response was very good and its response remained unchanged in the pH range of 6.0-9.0. The interference effect on the sensor response of different anionic species was tested by the separate solution method (SSM) and the sensor selectivity was quite good. The life time of the sensor was measured as 13 weeks and the sensor was successfully used as indicator sensor for the potentiometric titrations of iodide ions with silver nitrate solution. Additionally, the sensor was successfully applied for the direct detection of iodide ions in environmental water samples.

Keywords: Potentiometry, iodide selective sensor, potentiometric iodide determination, multiwalled carbon nanotube, environmental water analysis.

AgI-Cu_2S-Çok Duvarlı Karbon Nanotüp Malzeme Temelli Oldukça Seçici İyodür Sensör Kullanılarak İyodür İyonlarının Potansiyometrik Takibi

Öz

Bu çalışmada, iyodür iyonlarının oldukça seçici potansiyometrik tayini için gümüş iyodür (AgI) bakır(I) sülfür (Cu_2S) - Çok duvarlı karbon nano tüp (MWCNT) – Grafit (GO) - Parafin oil (PO) kompozit malzemesine dayalı yeni bir iyodür seçici sensör tanımlanmıştır. Sensörün en iyi potansiyometrik performans özelliklerini elde etmek için sensör bileşenleri optimize edilmiş ve optimize edilmiş sensör bileşenlerinin uygun şekilde preslenmesiyle sensör oluşturulmuştur. Deneysel sonuçlar, en uygun potansiyometrik cevabın 50:5:20:5:20 (% w/w) oranında G:MWCNT:AgI:Cu_2S:PO bileşimi içeren sensör kompozisyonu ile elde edildiğini göstermiştir. Geliştirilen sensör, iyodür iyonları için geniş bir doğrusal çalışma aralığı (1.0×10^{-5}–1.0×10^{-1} $molL^{-1}$) sergilemiştir. Bu doğrusal çalışma aralığında, sensörün Nernst eğimi 51.5±1.0 mV ve doğrusallık katsayısı (R^2) 0.9991 olarak belirlenmiştir. Sensörün cezap zamanı 5 saniye olarak ölçülmüştür. Sensörün potansiyel cevabının tekrarlanabilirliği çok iyiydi ve sensör cevabı pH=6.0-9.0 aralığında değişmeden kaldı. Farklı anyonik türlerin sensör cevabı üzerine girişim etkisi, ayrı çözelti yöntemi (SSM) ile test edildi ve sensör seçiciliğinin oldukça iyi olduğu gözlendi. Sensörün kullanım ömrü 13 hafta olarak belirlendi ve sensör, iyodür iyonlarının gümüş nitrat çözeltisi ile potansiyometrik titrasyonunda indikatör elektrot olarak başarıyla kullanıldı. Ayrıca sensör, çevresel su örneklerindeki iyodür iyonlarının doğrudan tayininde başarıyla uygulanmıştır.

Anahtar Kelimeler: Potansiyometri, iyodür seçici sensor, potansiyometrik iyodür tayini, çok duvarlı karbon nanotüp, çevresel su analizleri.

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1. Introduction

Iodine is an element with atomic number 53 in group 7A (halogens). Although it is in the group of chemically electronegative elements, iodine is the least electronegative element among the elements in the group and exists anionically in iodide form (I^-) [1, 2]. Iodine is mainly used in medicine, pharmacy, photography, paint industry. Animals, plants and humans need trace amounts of iodine. Iodine has many important functions such as enrichment of brain development, cell growth, energy metabolism, neurological functions and thyroid gland activity in human body. It is an important component of thyroxin and triiodothyronine which are among the thyroid hormones. Thyroid hormones regulate many biochemical reactions such as protein synthesis. Lack of iodine cause serious delays in neurological development. Additionally, excessive amounts of iodine and iodide give a start goiter and hypothyroidism illness [3-8]. Therefore, the monitoring of the iodine or iodide amount in natural waters and biological samples has a crucial importance.

A large number of analytical methods such as classical titrimetry [9], UV-VIS. spectrophotometry [10, 11], high pressure liquid chromatography (HPLC) [12], ion chromatography [13, 14] and voltammetry [15, 16] have been reported for the determination of iodide ions at low concentration levels. Most of the mentioned these methods are time consuming complicated techniques (except for classical titrimetry) and require expensive equipment, sample pretreatments and operational expertise. Thus, the sensitive, accurate, fast and reliable alternative methods for iodide determination have been attracting the attention of researchers.

The potentiometric determination of ionic species with ion selective sensors is one of the alternative methods. This method offers several advantages such as simple equipment, high selectivity, low cost, fast response and ease of application. Moreover, its applicability to turbid and colored solutions is one of the superior advantages of this method and are suitable for routine analysis of large number of clinical, biological, chemical, industrial and environmental samples [17-19].

In this paper, we described a highly selective and sensitive new iodide selective sensor based on an AgI-Cu$_2$S-Multiwalled carbon nanotube-Graphite-Paraffin oil composite material for the direct potentiometric monitoring of iodide ions. The optimization studies of the sensor components were carried out in detail and its potentiometric response characteristics were reported. The analytical performance in real sample analysis applications of the developed sensor was displayed by potentiometric titration of iodide ions with silver nitrate solution. In addition, the sensor was successfully applied for the direct detection of iodide ions in environmental water samples and the results obtained were evaluated as statistically.

2. Experimental

2.1. Reagents and chemicals

Silver nitrate, sodium iodide, copper(I) chloride, sodium sulphide and other all salts were purchased from Sigma-Aldrich. Multi-walled carbon nanotubes (50-90 nm diameter, > 95% carbon basis), reagent grade graphite powder (particle size <20 µm, synthetic), paraffin oil, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were provided from Sigma-Aldrich. During all experimental studies, the analytical grade chemicals and reagents were used and any further purification processes was not applied. Standard and stock solutions were prepared by using triply deionized-distilled water.

2.2. Apparatus

Potential data were recorded with a laboratory-made multi-channel potentiometric measurement system. The reference electrode used in the electrochemical system was a saturated calomel electrode (SCE) which obtained from Gamry Electrochemical Instruments. The pH adjustment of the test solutions was made by using Milwaukee Mi 150 pH/Temperature Bench Meter system. All homogenization processes were performed with IKA MS 3 D S000 digital stirrer system and Elma Elmasonic S 300H ultrasonic stirrer system. The weighing stages were carried out with Radwag AS 220.R2 Plus model analytical precision balance. The deionized-distilled water was supplied from ELGA Purelab Option-Q DV 25 water purification system.

2.3. Preparation of silver iodide and copper(I) sulphide

Silver iodide compound were prepared by stirring 0.1 $molL^{-1}$ 100 mL silver nitrate solution and 0.1 $molL^{-1}$ 100 mL sodium iodide solution. The formed precipitate was ripened by heating with an electronic heater and was filtered with a suitable filter paper. The filtrate was washed several times with deionized-distilled water and dried in an oven at 80 °C for 4 hours. The prepared silver iodide was kept at room temperature and in a closed and dark medium. Copper(I) sulphide compound were prepared by stirring 0.1 $molL^{-1}$ 100 mL copper(I) chloride solution and 0.1 $molL^{-1}$ 100 mL sodium sulphide solution. Then, the above described process steps were applied for copper(I) sulphide.

2.4. Preparation of iodide selective sensor

Iodide selective sensor was fabricated as follow: 20.0% (w/w) silver iodide (AgI), 5.0% (w/w) copper(I) sulphide (Cu_2S), 50.0% (w/w) graphite powder (G), 5.0% (w/w) multiwalled carbon nanotube (MWCNT) and 20.0% (w/w) paraffin oil (PO) were mixed and this mixture was completely homogenized for 60 minutes. This material was filled into a cylindrical plastic tube with 2.0 mm diameter and in 5.0 cm length. The plastic tube was pressed well from both ends during 24 h. After the pressing process is completed, a 1.0 cm long part of plastic tube was cut out and assembled on the end of a 15.0 cm long copper wire. The contact points were isolated by using a convenient adhesive and dried for 48 h at 20-25 °C. In this way, the construction of the iodide selective sensor was finalized. Before the potentiometric measurements, the iodide selective sensor was pre-conditioned during 2 h by dipping into 1.0×10^{-1} molL^{-1} standard sodium iodide solution. When the iodide selective sensor is not in use, it was waited at room temperature and in a closed and dark medium.

3. Results and Discussion

3.1. Optimization of sensor components

To obtain the best potentiometric sensing for the iodide ions, the use ratios of the sensor components were optimized in detail. For this purpose, several sensor compositions with different formulations were prepared by varying the amount of AgI and Cu_2S, multi walled carbon nanotube (MWCNT), graphite powder (G) and paraffin oil (PO). The potentiometric response of the sensor with the determined sensor formulations was tested against iodide ions. The measured sensor formulations for the optimization and theirs potentiometric response characteristics were summarized in Table 1. It is clearly seen in Table 1 that the sensor sensitivity for iodide ions raised with increasing of AgI. The optimum AgI ratio was determined as 20.0% (w/w). When the AgI was increased by more than 20.0%, a decrease in the sensor response was observed. This is probably due to the maximum interaction of the AgI with iodide ions in this ratio. It is declared that the sensor conductivity is improved by using multi-walled carbon nanotubes (MWCNT) in the composition of ion sensors. Therefore, we preferred to use multi-walled carbon nanotubes (MWCNT) in the sensor composition. The obtained experimental results displayed that the use of 5.0% (w/w) MWCNT in the sensor composition contributed to the improvement of the sensor response. Consequently, among the compositions examined, the optimum sensor composition was determined as 20.0% (w/w) AgI, 5.0% (w/w) copper(I) sulphide (Cu_2S), 50.0% (w/w) graphite powder (G), 5.0% (w/w) multiwalled carbon nanotube (MWCNT) and 20.0% (w/w) paraffin oil (PO). In the rest of this study, all potentiometric tests and the real sample analysis applications were made by using the sensor with the optimized composition [20-23].

Table 1. The tested sensor formulations for the optimization and theirs potentiometric performance characteristics.

No	Sensor Composition, (w/w) %, mg					Linear Working Range (molL^{-1})	Slope (mV/decade of concentration)	R^2	Response Time (s.)
	AgI	Cu_2S	Graphite (G)	Multiwalled Carbon nanotube (MWCNT)	Paraffin Oil (PO)				
1	10.0	-	70.0	-	20.0	1.0×10^{-3} – 1.0×10^{-1}	15.8±3.4	0.6628	75
2	15.0	-	65.0	-	20.0	1.0×10^{-3} – 1.0×10^{-1}	23.4±2.8	0.8246	59
3	20.0	-	60.0	-	20.0	1.0×10^{-4} – 1.0×10^{-1}	36.2±2.1	0.9099	41
4	25.0	-	55.0	-	20.0	1.0×10^{-3} – 1.0×10^{-1}	24.6±2.0	0.8546	48
5	20.0	2.5	57.5	-	20.0	1.0×10^{-4} – 1.0×10^{-1}	41.8±1.6	0.9327	33
6	20.0	5.0	55.0	-	20.0	1.0×10^{-4} – 1.0×10^{-1}	46.6±1.5	0.9579	27
7	20.0	7.5	52.5	-	20.0	1.0×10^{-4} – 1.0×10^{-1}	40.8±1.8	0.9224	39
8	20.0	5.0	52.5	2.5	20.0	1.0×10^{-4} – 1.0×10^{-1}	48.9±1.5	0.9688	11
9	20.0	5.0	50.0	5.0	20.0	1.0×10^{-5} – 1.0×10^{-1}	51.5±1.0	0.9991	5
10	20.0	5.0	47.5	7.5	20.0	1.0×10^{-5} – 1.0×10^{-1}	48.5±1.3	0.9781	15
11	20.0	5.0	55.0	5.0	15.0	1.0×10^{-4} – 1.0×10^{-1}	45.4±1.8	0.9526	26
12	20.0	5.0	60.0	5.0	10.0	1.0×10^{-3} – 1.0×10^{-1}	37.8±2.3	0.9021	43
13	20.0	5.0	45.0	5.0	25.0	1.0×10^{-4} – 1.0×10^{-1}	41.2±1.7	0.9428	33
14	20.0	5.0	40.0	5.0	30.0	1.0×10^{-3} – 1.0×10^{-1}	44.5±1.6	0.7451	56

3.3. Potentiometric response of iodide selective sensor

After the optimization of the sensor components, the potentiometric response of the sensor was evaluated against both iodide ions and other selected anions. All of the test solutions were prepared in equal concentration (1.0×10^{-5}-1.0×10^{-1} molL^{-1}) at pH=6.0. The ionic strength adjustments and the calculating of the activity coefficient (γ) values of the test solutions were made as the mentioned procedure in our previous study [24, 25]. The iodide selective sensor was directly dipped into each test solution. After the sensor reached its equilibrium response, the potential values was saved. In the transition from one solution to another, the sensor surface was thoroughly washed with deionized-distilled water. After the tests were completed, a potential (mV) – log C (molL^{-1}) graph (Figure 1) was created by using the attained all data. As clearly seen from Figure 1, the fabricated iodide selective sensor was showed a highly selective and sensitive potentiometric response to iodide ions. The potentiometric response of the sensor for iodide ion was very close to the theoretical Nernst answer in which the slope is 59.2 mV per decade for the univalent anions.

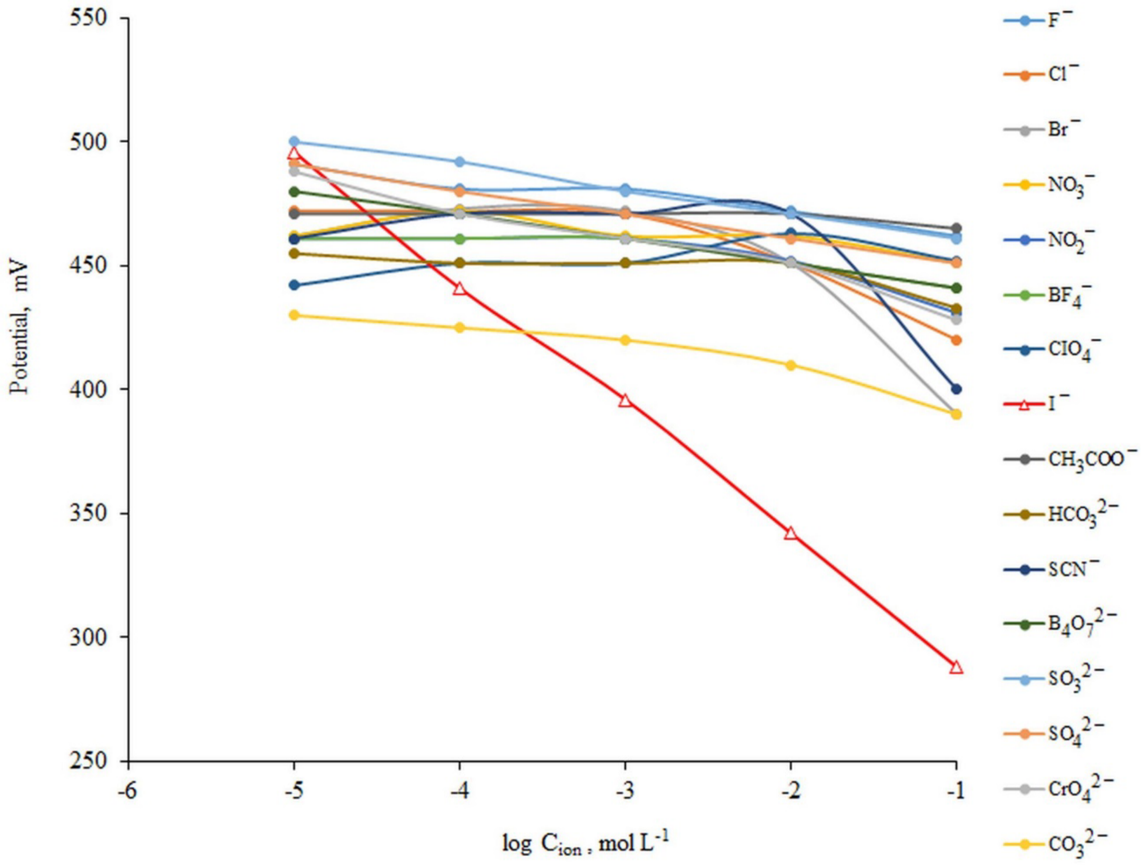

Figure 1. Potentiometric response of the iodide selective sensor to iodide ion and other anions.

After this stage, the important potentiometric performance characteristics such as linear working range, detection limit and slope of the iodide selective sensor were determined with the further calibration studies. By using the standard iodide solutions in the concentration range of 1.0×10^{-8}-1.0×10^{-1} molL^{-1} (pH=6.0), the advanced calibration measurements were performed with the iodide selective sensor. The potentiometric measurements (Figure 2) indicated that the developed sensor was of a wide linear working range for iodide ions over the concentration range of 1.0×10^{-5}-1.0×10^{-1} molL^{-1} (R^2=0.9991). In this linear working range, the experimental Nernstian slope of the sensor was 51.5±1.0 mV/decade and this slope value was very close to the theoretical Nernstian slope value (59.2 mV/decade for monovalent ions). The detection limit of the sensor was found as 9.0×10^{-6} molL^{-1} [24, 25].

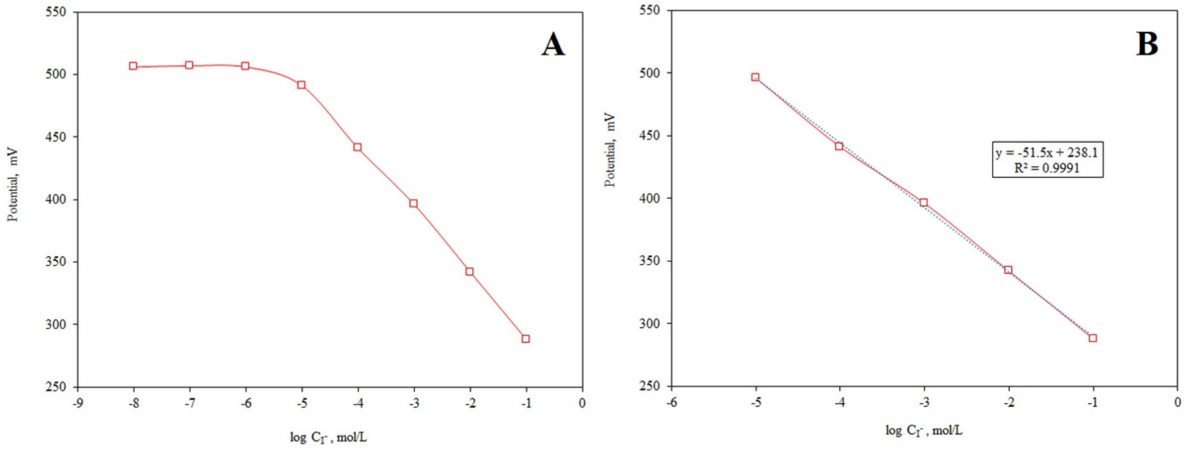

Figure 2. Wide calibration plot (A) and linear working range (B) of the iodide selective sensor.

3.4. Selectivity and Interference Studies

The interference effect in the ion sensors is an important factor for analytical applications. In our study, the selectivity of the fabricated sensor was studied by separate solution method (SSM). The selectivity coefficient values of the sensor were calculated by separately measuring the target ion (I^-) and other monovalent and bivalent anionic species including F^-, Cl^-, Br^-, NO_3^-, NO_2^-, BF_4^-, ClO_4^-, CH_3COO^-, HCO_3^-, SCN^-, $B_4O_7^{2-}$, SO_3^{2-}, SO_4^{2-}, CrO_4^{2-} and CO_3^{2-}. The results obtained were given in Table 2. As shown in Table 2, the developed iodide selective sensor exhibited a high selectivity for reliable potentiometric measurement of iodide ions in the presence of various interfering ions. According to the calculated selectivity coefficient values, the highest interference to the potentiometric response of the sensor was caused by nitrite ions (NO_2^-). Even in this case, the iodide selective sensor exhibited approximately 110 times more selective behavior towards target ions [3, 26, 27].

Table 2. Selectivity coefficients of the iodide selective sensor.

Seperate Solution Method (SSM)

Interfering ion	Selectivity Coefficient $K_{A,B}^{pot}$	Logarithmic Selectivity Coefficient $-\log K_{A,B}^{pot}$
NO_2^-	$9.13x10^{-3}$	2.04
HCO_3^-	$8.52x10^{-3}$	2.07
SO_4^{2-}	$1.67x10^{-3}$	2.78
Br^-	$1.54x10^{-3}$	2.81
CH_3COO^-	$1.18x10^{-3}$	2.93
SCN^-	$1.18x10^{-3}$	2.93
Cl^-	$1.13x10^{-3}$	2.95
NO_3^-	$1.06x10^{-3}$	2.98
CO_3^{2-}	$1.06x10^{-3}$	2.98
CrO_4^{2-}	$7.92x10^{-4}$	3.10
SO_3^{2-}	$7.41x10^{-4}$	3.13
F^-	$5.02x10^{-4}$	3.30
$B_4O_7^{2-}$	$2.02x10^{-4}$	3.70
BF_4^-	$7.42x10^{-4}$	4.13
ClO_4^-	$3.17x10^{-5}$	4.50

3.5. Effect of pH

In order to determine the effect of pH on the sensor response, a study of the monitoring of sensor potentials at different pH values was carried out by using 1.0×10^{-2} and 1.0×10^{-3} $molL^{-1}$ standard iodide solutions. The pH values of the standard iodide solutions was adjusted with a very small drop of dilute hydrochloric (HCl) acid and sodium hydroxide solutions (NaOH). While the iodide ion concentration was kept constant in the solution, the pH values of the solutions were changed between 2.0-12.0. The potentials of the pH adjusted solutions were monitored with the iodide selective sensor and the obtained potential data were used to plot the potential-pH graph (Figure 3). As seen in Figure 3, the potential response of the developed iodide selective sensor was stable between pH=6.0-9.0. At pH<6.0, a gradually increase in the sensor potentials was observed. The observed this drift in the sensor response may be explained with the interference effect of the high rate of diffusion of hydronium ions from test solution to sensor matrix. At pH values higher than pH=9, the decrease in the sensor potential values is probably due to the sensor's response to hydroxyl ions [25, 28].

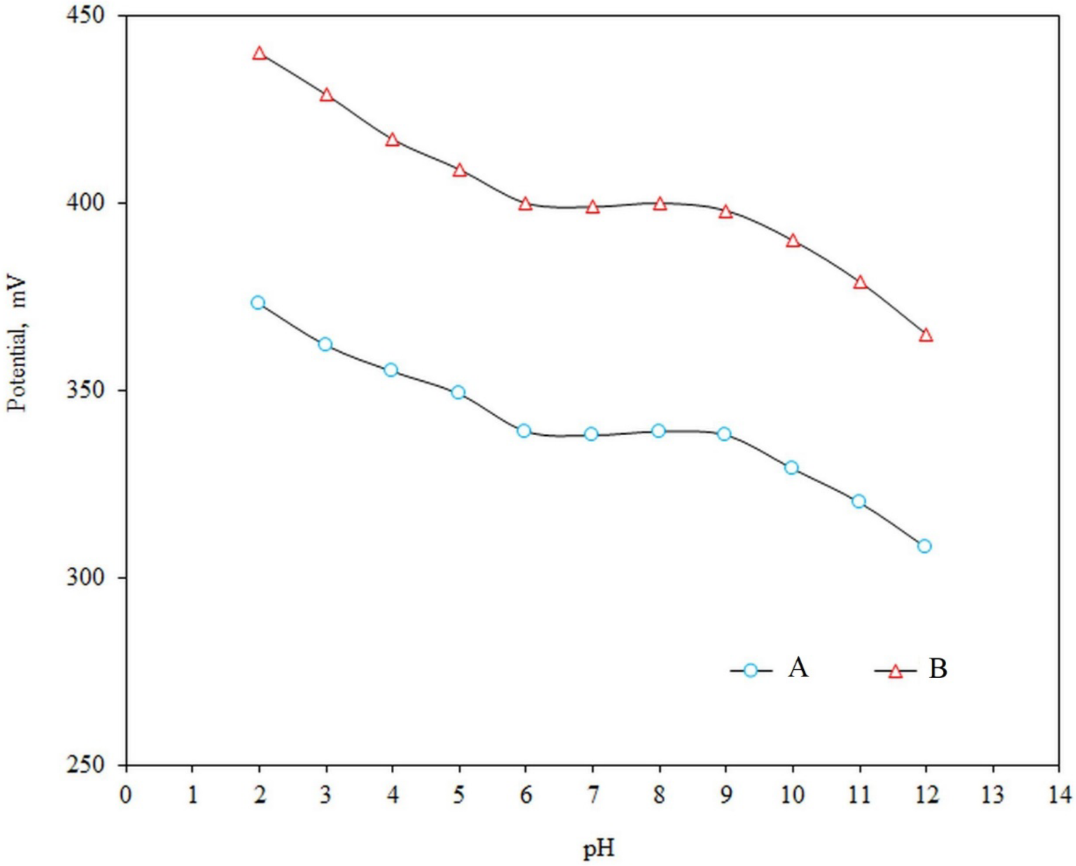

Figure 3. Effect of pH on response of the iodide selective sensor (A: 1.0×10^{-3} and B: 1.0×10^{-2} molL^{-1} I$^-$).

3.6. Response time

Response time is an important potentiometric performance property in the ion sensors and defined as the elapsed time to achieve 95% of the equilibrium potential of the sensor. In this study, the response time of the sensor was assessed in the standard iodide solutions over the concentration range of 1.0×10^{-4} to 1.0×10^{-1} molL^{-1}. The array of potential measurements was chosen such that the higher I$^-$ concentration from the lower I$^-$ concentration. The results in Figure 4 demonstrated that the developed sensor reached its final potential very quickly and the average response time of the sensor was measured as 5 seconds in all concentration range [29, 30].

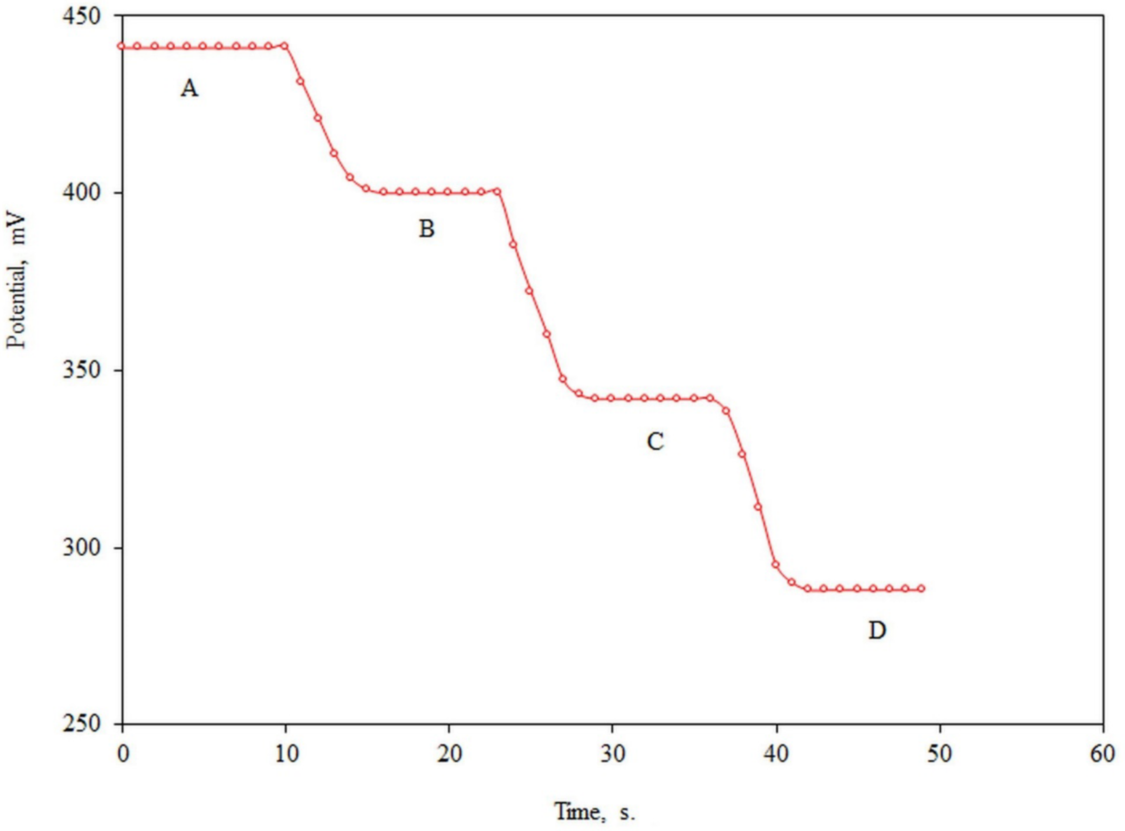

Figure 4. Dynamic response time of the iodide selective sensor (A: 1.0×10^{-4}, B: 1.0×10^{-3}, C: 1.0×10^{-2} and D: 1.0×10^{-1} molL^{-1} I^{-}).

3.7. Repeatability and Life time

The repeatability of the sensor potentials was tested by alternately monitoring the potential response of the iodide selective sensor in standard iodide test solutions (1.0×10^{-4}, 1.0×10^{-3}, and 1.0×10^{-2} molL^{-1}). The obtained potential data reveal that the developed iodide selective sensor was exhibited a highly reversible and repeatable potentiometric response. The experimental repeatability results of the sensor were given in Figure 5. The standard deviations of measurements were calculated as ±1.0, ±1.0 and ±1.1 mV for 1.0×10^{-2}, 1.0×10^{-3} and 1.0×10^{-4} molL^{-1} I^{-}, respectively [20, 21].

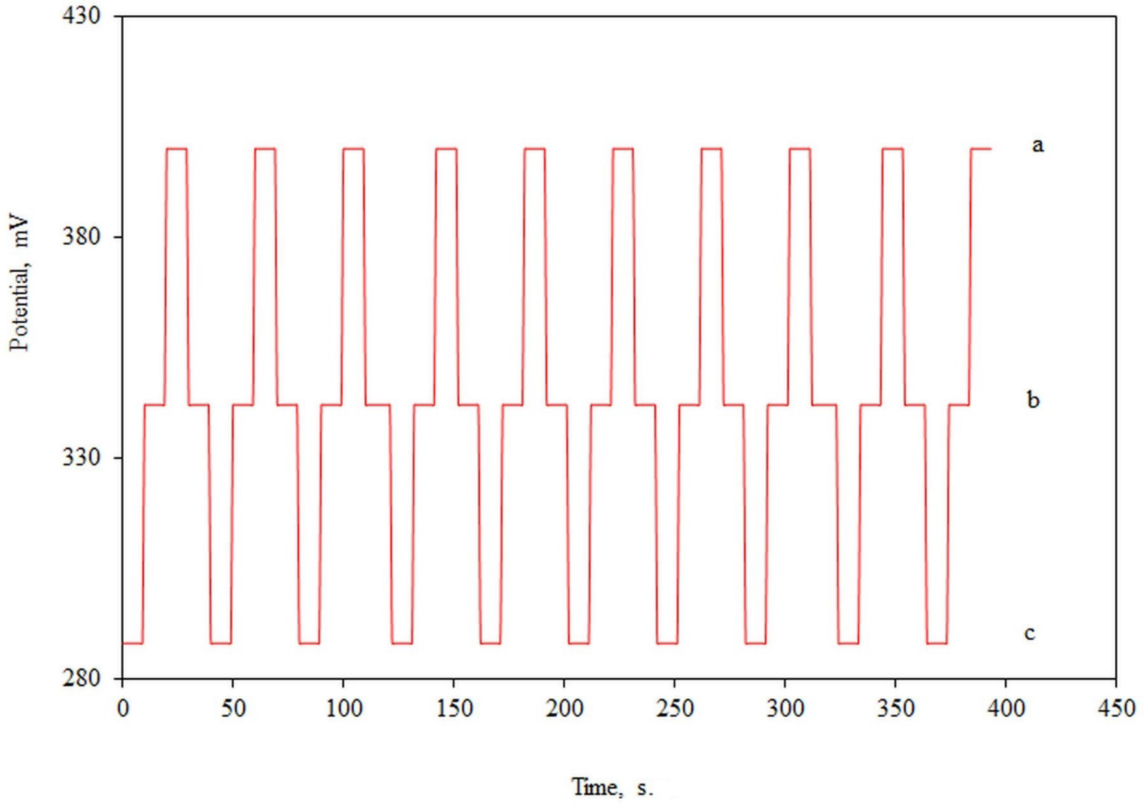

Figure 5. Repeatability of the potential response of the iodide selective sensor (a: 1.0×10^{-2}, b: 1.0×10^{-3} and c: 1.0×10^{-4} $\mathrm{molL^{-1}}$ I^{-}).

The life time of the iodide selective sensor was detected with the periodic calibration measurements for 16 weeks. In this period, the same iodide selective sensor was used and weekly calibration measurements were carried out. The attained potentiometric slope values were recorded and a slope-time graph ((Figure 6) were plotted. When the data in Figure 6 was examined, it is clearly seen that the iodide selective sensor was successfully used for 13 weeks without any significant change in the sensor response. During the 13 weeks, the Nernstian slope of the iodide selective sensor did not change by more than ±1.0 mV and the potentiometric performance characteristic such as detection limit, response time, selectivity and pH working range was almost at the same values. After the 13th week, the detection limit and response time of the sensor was gradually reduced with time. Therefore, the optimum life time of the sensor was determined as 13 weeks [20, 21].

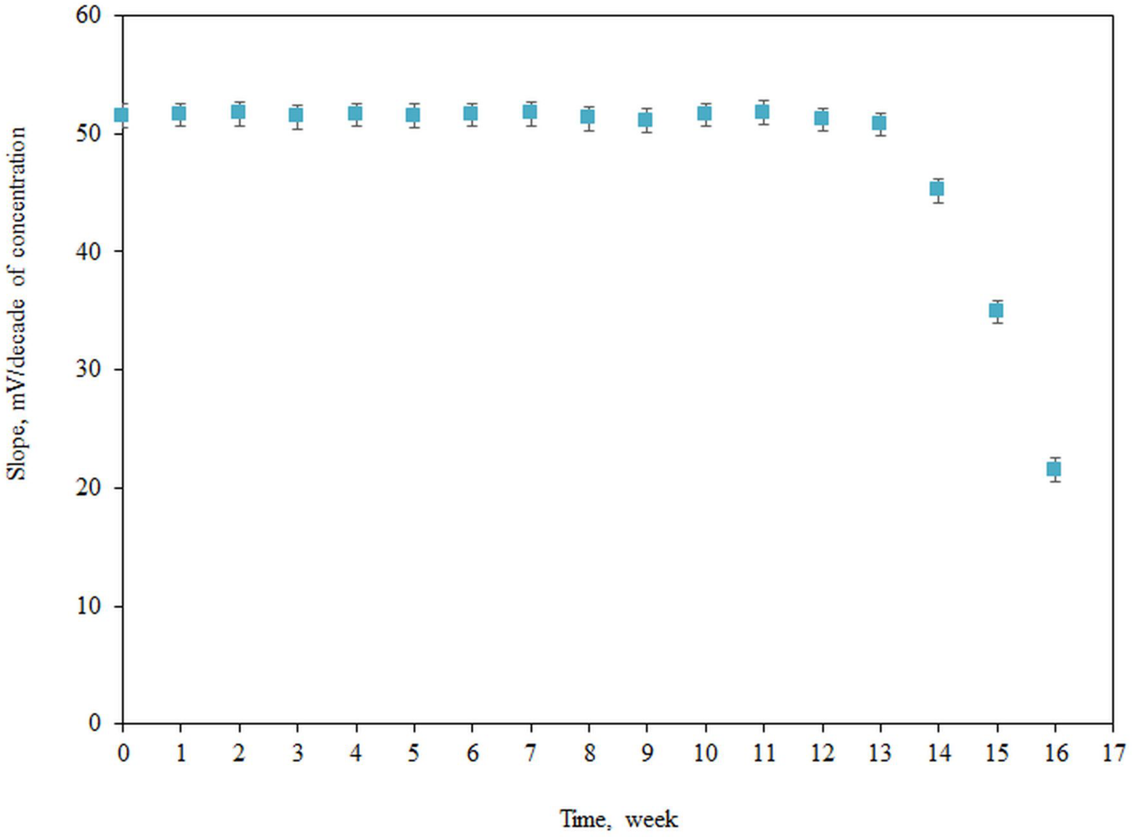

Figure 6. Life time of the iodide selective sensor.

3.8. Comparison study

In our work, we compared the potentiometric performance characteristics of the proposed sensor with the previously reported iodide selective sensors. The comparison results are given in Table 3. As obviously seen in Table 3, some potentiometric response characteristics such as linear working range, Nernstian slope, detection limit, and response time of the developed sensor are better than similar sensors in the literature. The most important feature of the proposed sensor that distinguishes it from other similar sensors available in the literature is that its response time is very short (5 s.).

Table 3. Comparison of potentiometric performance characteristics of the present sensor with the reported sensors in literature.

Reference No	Linear working range ($molL^{-1}$)	Detection limit ($molL^{-1}$)	Slope (mV/Decade of activity)	Response time (s.)	pH range	Lifetime (mounth)
[4]	1.0×10^{-6}-1.0×10^{-1}	6.0×10^{-7}	56.85	NM	NM	NM
[5]	1.0×10^{-7}-1.0×10^{-1}	8.0×10^{-8}	57.6±0.8	0,5	2.0-11.5	2
[6]	2.5×10^{-7}-1.5×10^{-3}	0.1 ($\mu molL^{-1}$)	NM	NM	4.0-8.0	6
[7]	1.0×10^{-6}-1.0×10^{-1}	6.0×10^{-7}	58.4±1.4	≤10	3.5-11.5	2
[8]	1.0×10^{-6}-1.0×10^{-1}	7.0×10^{-7}	58.9±0.9	≤50	3.0-11.0	2
[18]	9.2×10^{-7}-1.0×10^{-1}	8.5×10^{-7}	58.9±1.5	3	3.0-8.0	2
[19]	5.0×10^{-6}-1.0×10^{-1}	1.0×10^{-6}	57.1±1.8	20	3.0-8.0	1
[22]	8.0×10^{-7}-1.0×10^{-1}	2.0×10^{-7}	60.2	15	5.5-8.0	3
[28]	5.0×10^{-6}-2.0×10^{-1}	1.0×10^{-6}	56.8	10	3.0-9.0	NM
[32]	1.0×10^{-5}-1.0×10^{-2}	7.0×10^{-6}	59.8±0.5	<20	2.5-8.5	6 (week)
This work	1.0×10^{-5}-1.0×10^{-1}	9.0×10^{-6}	51.5.7±1.0	5	6.0-9.0	13 (week)

NM: not mentioned.

3.9. Analytical applications

The utility of the iodide selective sensor was investigated with the potentiometric titration of iodide ions with silver nitrate solution. A 1.0×10^{-3} $molL^{-1}$ 25 mL iodide solution was titrated with 1.0×10^{-3} $molL^{-1}$ silver nitrate solution and the end point of the potentiometric titration was determined by using the proposed iodide selective sensor. A 100 µL of titrant solution (silver nitrate) was added each time onto the analyte solution (iodide solution). A titration plot was created with the obtained potentiometric data. As can be seen in Figure 7, the titration curve was of a conventional sigmoidal shape and the silver ions in the silver nitrate solution formed a 1:1 stoichiometric complex with the iodide ions in the iodide solution. The end point of the potentiometric titration was 24.0±1.0 mL and the developed iodide selective sensor was successfully used as an indicator electrode in the potentiometric titration [31, 32].

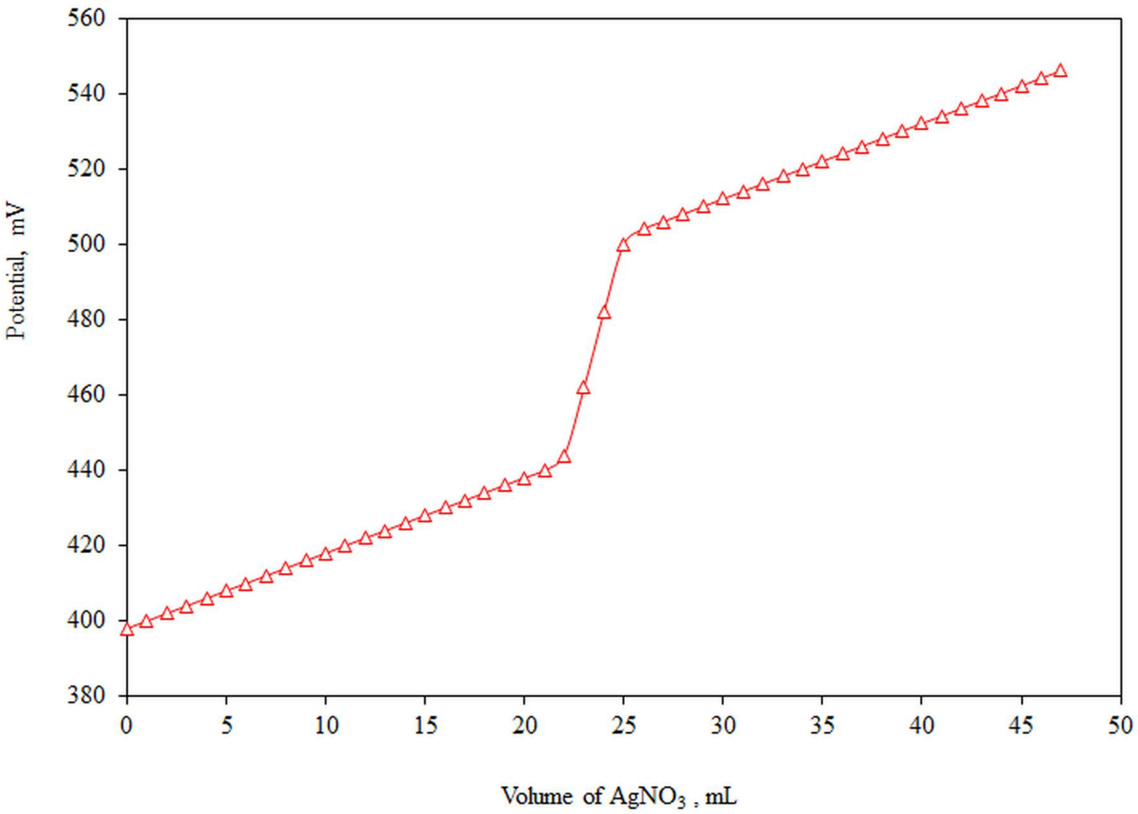

Figure 7. Potentiometric titration of 25 mL of 1.0×10^{-3} molL^{-1} I$^-$ with 1.0×10^{-3} molL^{-1} silver nitrate solution using the iodide selective sensor.

Additionally, the developed sensor was applied to the direct potentiometric determination of iodide ions in spiked different water samples such as dam water, river water and tap water. River water samples were collected from the Kızılırmak River in Bafra, Samsun. Dam water samples were provided from the Derbent Dam Lake in Bafra, Samsun. Tap water samples were obtained from our research laboratory in Ondokuzmayıs, Samsun. The whole water samples were filtrated through 0.45 µm poly-tetra fluoro ethylene (PTFE) filters to eliminate the insoluble particles. The spiked iodide ion concentrations and obtained potentiometric data were summarized in Table 4. As seen in Table 4, the results were in very good agreement with theoretical results. As a results, the developed sensor could be successfully used in the direct determination of iodide amount in different water samples.

Table 4. Determination of iodide content in spiked different water samples.

a

Sample	Added I^- (ppm)	[a]Found by Sensor I^- (ppm)	Relative error (%)	Recovery (%)
Tap water	126.90	125.80±0.90	0.87	99.13
Tap water	63.45	62.70±1.10	1.18	98.82
Tap water	12.69	12.40±1.26	2.28	97.72
River water	126.90	126.10±0.60	0.63	99.37
River water	63.45	62.90±1.08	0.87	99.13
River water	12.69	12.48±1.14	1.65	98.35
Dam water	126.90	126.40±0.40	0.40	99.60
Dam water	63.45	63.10±0.56	0.55	99.45
Dam water	12.69	12.56±0.88	1.02	98.98

The mean and standard deviation values are given for n=5.

4. Conclusions

A novel iodide selective sensor based on an AgI-Cu_2S-Multiwalled carbon nanotube-Graphite-Paraffin oil composite material was successfully fabricated and examined the important potentiometric performance characteristics of its. The prepared sensor had a very selective and sensitive potentiometric response to iodide ions. The sensor having the optimized composition (20.0% (w/w) AgI, 5.0% (w/w) copper(I) sulphide (Cu_2S), 50.0% (w/w) graphite powder (G), 5.0% (w/w) multi walled carbon nanotube (MWCNT) and 20.0% (w/w) paraffin oil (PO)) gave the best potentiometric performance characteristics (linear range: 1.0×10^{-5} - 1.0×10^{-1} $molL^{-1}$, Nernstian slope: 51.5±1.0 mV, $R^2=0.9991$ and detection limit: 9.0×10^{-6} $molL^{-1}$). The developed sensor exhibited a very fast response time (5s) and revealed a highly reversible and repeatable potential response to iodide ions. The sensor response remained unchanged in the pH range of 6.0-9.0 and the selectivity of the sensor against different anionic species was very good. The potentiometric response of the sensor was stable for 13 weeks. The sensor could be used as an indicator sensor for the potentiometric titrations of iodide ions with silver nitrate solution and could be successfully applied for the direct determination of iodide content in different water samples without the requirement for any pre-concentration or pre-treatment steps.

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