

Highly Selective Direct Determination of Sunset Yellow Using a Novel Polymeric Membrane Sensor Containing Metal Organic Framework Material

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Abstract

In this study, a novel polymeric membrane potentiometric sensor based on metal organic framework was presented for the direct determination of sunset yellow. The sensor was fabricated using different ratios of sensor components containing metal organic framework (MIL-101), polyvinylchloride, nitrophenyloctylether, bis-2-ethylhexylsebecate, dibutylphthalate, and potassiumtetrakischlorophenylborate. The sensor components were optimized to obtain the best potentiometric response and the most desired response characteristics were achieved with the sensor composition including 6.0% ionophore (MIL-101), 26.0% polyvinylchloride, 67.0% dibutylphthalate and 1.0% potassiumtetra-p-chloro-phenylborate. The optimized sensor showed a linear response to sunset yellow over the concentration range of 1.0×10^{-6} - 1.0×10^{-1} molL⁻¹ ($R^2=0.9993$) with a Nernstian slope of 35.7 ± 0.5 mV/decade and the detection limit was calculated as 1.7×10^{-7} molL⁻¹. The sensor response was highly repeatable, and its response time was measured as 5s on average. The sensor's potential response was not affected by the change of hydronium ions in the solution between pH=5.40-9.55 and its lifetime was evaluated as 14 weeks. The sensor was used as an indicator electrode in the titration of sunset yellow with silver nitrate solution. Additionally, the usefulness for the analytical applications of the sensor were tested using the sunset yellow spiked different water samples and some pharmaceutical drug formulations.

Keywords: Sunset yellow, metal organic framework, electrochemistry, sensors, water and pharmaceutical drug analysis.

Metal Organik Framework Materyal İçeren Yeni Bir Polimerik Membran Sensör Kullanılarak Sunset Yellow'un Oldukça Seçici Doğrudan Tayini

Öz

Bu çalışmada, sunset yellow'un doğrudan tayini için metal organik framework temelli yeni bir polimerik membran potansiyometrik sensör sunulmuştur. Sensör, metal organik framework (MIL-101), polivinilklorür, nitrofeniloktiller, bis-2-etilhegzilsebekat, dibutilftalat ve potasyum tetrakis-klorofenilborat içeren sensör bileşenlerinin farklı oranları kullanılarak üretildi. Sensör bileşenleri en iyi potansiyometrik cevabı elde etmek için optimize edildi ve en arzu edilen cevap özelliklerine % 6,0 iyonofor (MIL-101), % 26,0 polivinilklorür, % 67,0 dibutilftalat ve % 1,0 potasyum tetra-p-kloro-fenilborat içeren sensör bileşimi ile ulaşıldı. Optimize edilen sensör, $35,7 \pm 0,5$ mV'luk Nernstian eğimi ile $1,0 \times 10^{-6}$ - $1,0 \times 10^{-1}$ molL⁻¹ ($R^2=0,9993$) konsantrasyon aralığında sunset yellow'a karşı doğrusal bir cevap sergiledi ve tayin limiti $1,7 \times 10^{-7}$ molL⁻¹ olarak belirlendi. Sensör cevabı oldukça tekrarlanabilirdi ve sensörün cevap zamanı ortalama 5 saniye olarak ölçüldü. Sensörün potansiyel cevabı, pH=5,40-9,55 arasında çözeltideki hidronyum iyonlarının değişiminden etkilenmedi ve sensörün kullanım ömrü 14 hafta olarak belirlendi. Sensör, sunset yellow'un gümüş nitrat çözeltisi ile titrasyonunda indikatör elektrot olarak kullanıldı. Ayrıca, sensörün analitik uygulamalarda kullanılabilirliği, standart sunset yellow eklemesi yapılmış farklı su örneklerinde ve bazı farmasötik ilaç formülasyonlarında test edildi.

Anahtar Kelimeler: Sunset yellow, metal organik framework, elektrokimya, sensörler, su ve farmasötik ilaç analizi.

1. Introduction

Synthetic food dyes commonly used in the food and beverage industry today serve to enhance the aesthetic appearance of products and increase consumer appeal [1, 2]. They contribute to the creation of preferred products by imparting various color tones and visual characteristics to food items and beverages [3]. However, due to the azo-functional group ($-N=N-$) and aromatic ring in their structure, some of these color additives may raise health concerns and have adverse effects when consumed excessively [4]. Therefore, the control and detection of color additives used in the food and beverage industry are of great importance.

Sunset Yellow (SY) is one of the most important artificial coloring agents used in foods and beverages [5]. This synthetic food coloring agent is employed to enhance the visual appeal of food and beverage products and improve their colors. It is often used as a preferred colorant in orange-colored products and beverages. Additionally, it can be found in a variety of food products including sweets, confectionery, various beverages (such as fruit juices and carbonated drinks), ice cream, puddings, jellies, jams, and some soup varieties [6, 7]. Apart from its color-giving properties, sunset yellow (SY) is also used to improve the aesthetic appearance of food products. However, artificial colorants such as Sunset Yellow can potentially induce allergic reactions or sensitivities in some individuals, and when consumed excessively, they can lead to serious health problems such as anxiety, vomiting, diarrhoea, allergies, decreasing thymus weight, gastric annoyance, kidney and liver disorders [5, 8, 9]. Therefore, the presence and content of synthetic food dye additives like Sunset Yellow in food products is of great importance and should be controlled with rapid and sensitive analytical methods or techniques.

Several advanced analytical methods and techniques including spectrophotometry [10, 11], capillary electrophoresis [12, 13], high performance liquid chromatography (HPLC) [14-16], thin-layer chromatography (TLC) [17], liquid chromatography (LC) [18], and solid-phase extraction method [19] for determination of Sunset Yellow have been reported in literature. Although the present methods and techniques have high accuracy and sensitivity for the SY determination, they comprise some drawbacks such as consumption of a large amount of hazardous reagents/chemicals, high-cost chemical and/or equipment requirement, time-consuming sample pre-treatment procedures and necessity of trained/experienced device operators. Therefore, it is an important requirement to develop and improve new analytical methods to overcome the above-mentioned disadvantages of existing methods and techniques in the determination of Sunset Yellow.

Ion sensors show great advantages thanks to their superior features such as miniaturization, portability, ease of use, simple instrumentation, requiring very small amounts of sample, ease of preparation, applicability to colored and turbid samples, high selectivity/sensitivity and ability to detect at very low levels, short response time [6, 8, 9]. Especially, owing to the electroactive molecule (ionophore) in the sensor structure that exhibits

selective and sensitive behavior towards the target analyte, much more sensitive and stable sensors can be developed.

This study focuses on the development of a new potentiometric sensor for the highly selective direct determination of Sunset Yellow. For the first time, this sensor is designed by using Metal Organic Framework (MOF) materials, leveraging their unique porous structures, high surface areas, and selective binding properties to enhance detection performance [20, 21]. The work investigates systematically the design, production, and characterization of the MOF-based sensor, exploring its potential for the direct detection of Sunset Yellow with high sensitivity and selectivity. Furthermore, the results of this study may contribute to the development of more reliable and efficient analytical methods for monitoring Sunset Yellow and similar color additives in the food and beverage industry. Additionally, the findings underscore the potential of MOF-based sensors in terms of monitoring and controlling such additives, which are crucial for food safety and consumer health.

2. Material and Methods

2.1. Chemicals and Solutions

All chemicals used in the experimental studies were reagent grade chemicals and were purchased from Sigma Aldrich. Standard and stock solutions were daily prepared from high purity nitrate solutions of the related cations. All solution preparation and dilution procedures were performed using the deionized-distilled water. Experimental stock solutions were stored in the dark when not in use.

2.2. Apparatus

The silver/silver chloride electrode was used as reference electrode in all potentiometric measurements and was purchased from Gamry Electrochemical Instruments. Potentiometric data were collected with a laboratory-made, computer-controlled, high-input impedance, multichannel potentiometric measurement system. pH measurements were made by using Orion Star A215 model pH/Conductivity meter. All experimental studies were performed at room temperature (25 °C).

2.3. Preparation of electroactive material (MIL-101)

MOF-based electroactive material (MIL-101) used in the sensor structure was synthesized according to the previously reported method in literature [22, 23]. A 2.0 g (5 mmol) of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.83 g (5 mmol) of terephthalic acid were mixed in 20 mL of deionized-distilled water. This mixture was sonicated for a short time and a dark blue suspension with pH 2.58 was obtained. The obtained dark blue suspension was transferred to Teflon cover and kept unstirred in an oven at 218 °C for 18 h. Then, the mixture was stirred at 5000 rpm for 10 minutes and the solid particles were separated from the supernatant by centrifugation. The precipitate was washed with both deionized-distilled water and methanol. The resulting product was recrystallized in acetone solution. The acetone solution was evaporated and 20 mL of N,N-

dimethylformamide was added onto the remaining precipitate. The mixture was sonicated for 10 minutes and then kept at 70°C for 24 h. The resulting particles were separated by centrifugation and washed repeatedly with methanol and acetone. Finally, the obtained final particles were dried under vacuum at 80 °C for 1 day.

2.4. Preparation of PVC-membrane sunset yellow selective sensor

PVC-membrane sunset yellow selective sensors were prepared by systematically following the mentioned steps below:

Firstly, a polymeric membrane mixture was prepared by dissolving 12.0 mg of the synthesized electroactive material (MIL-101), 52.0 mg of polyvinyl chloride (PVC), 134.0 mg of dibutyl phthalate (DBP), and 1.0 mg of potassiumtetrakischlorophenylborate (KTpClPB) in 1.5 mL tetrahydrofuran (THF). Later, a copper wire of 15.0 cm length and 1.0 mm width was taken as the sensor substrate. One end of this copper wire was used as the device connection point, and the other end was coated with the prepared polymeric sensor mixture. Before the coating procedure of the polymeric sensor mixture, in this point of the copper wire, a conductive and rough surface was created by coating with the solid contact sensor material consisting of 100.0 mg of graphite, 70.0 mg of epoxy, 30.0 mg of hardener and 2 mL of tetrahydrofuran (THF). The created conductive solid contact surface was covered with the prepared polymeric membrane mixture by sinking 4-5 times. Finally, the sensor coated with a polymeric membrane mixture was kept in a dark and dry medium at room temperature. Before using the sensor, it was conditioned for at least 1 hour by dipping into $1.0 \times 10^{-1} \text{ molL}^{-1}$ standard sunset yellow solution [6, 24].

3. Results and Discussion

3.1. Optimization of the sensor components

In the sensor studies, to obtain the most desirable potentiometric responses such as high sensitivity, satisfying selectivity, wide linear dynamic range and fast response time from the sensor, the sensor components need to be optimized [25-27]. In the present study, we determined the optimal composition of the sensor components by measuring the potential response of sensors with different compositions. For this purpose, the polymeric membrane cocktails containing different ratios of MIL-101, PVC, NPOE, DOS, DBP, and KTpClPB were prepared and the PVC-membrane sunset yellow selective sensors with various compositions were produced using these membrane cocktails. The potentiometric response of sensors with different compositions was tested in the standard sunset yellow solutions over the concentration range of 1.0×10^{-7} - $1.0 \times 10^{-1} \text{ molL}^{-1}$ (in Tris HCl buffer solution at pH=7.50). The tested sensor compositions in the optimization experiments and the potentiometric response characteristics of theirs were detailed in Table 1. As seen in Table 1, the sensitivity of the sensor against sunset yellow rose with the increase in the use of MIL-101 in the sensor structure and reached the optimum value at 6.0% (w/w). This is likely due to the optimum interaction of the MIL-101 with sunset yellow in this ratio. When the MIL-101 in the sensor structure increased by more than 6.0%, it was observed that there were serious decreases in the sensor response. Therefore,

the optimum MIL-101 content of the sensor was determined as 6.0% (w/w). It is stated that the sensor selectivity towards target analyte is increased by using KTpClPB in the composition of ion sensors. Therefore, we preferred to use KTpClPB in sensor composition. The attained experimental data showed that the use of 1.0% (w/w) KTpClPB in the sensor membrane composition contributed to the improvement of the sensor response. Consequently, the optimum sensor composition was determined as 6.0% MIL-101, 26.0% PVC, 67.0% DBP and 1.0% KTpClPB. After this stage, all potentiometric performance tests and the real sample analysis applications were carried out by using the polymeric membrane sunset yellow selective sensor prepared with the optimized sensor composition.

Table 1. Tested sensor compositions and its response characteristics.

Sensor No	Sensor composition, w/w % (mg)						Linear Range (molL ⁻¹)	Slope (mV/decade of concentration)	R ²	Response Time (s)
	Ionophore	PVC	NPOE*	DOS*	DBP	KTpClPB				
1	4.0	26.0	70.0	-	-	-	1.0×10 ⁻³ – 1.0×10 ⁻¹	15.7	0.9125	24
2	4.0	26.0	-	70.0	-	-	1.0×10 ⁻³ – 1.0×10 ⁻¹	18.3	0.9348	19
3	4.0	26.0	-	-	70.0	-	1.0×10 ⁻⁴ – 1.0×10 ⁻¹	20.4	0.9675	15
4	4.0	26.0	-	-	69.5	0.5	1.0×10 ⁻⁴ – 1.0×10 ⁻¹	23.6	0.9857	11
5	4.0	26.0	-	-	69.0	1.0	1.0×10 ⁻⁴ – 1.0×10 ⁻¹	26.7	0.9892	9
6	4.0	26.0	-	-	68.5	1.5	1.0×10 ⁻⁴ – 1.0×10 ⁻¹	26.4	0.9868	10
7	5.0	26.0	-	-	68.0	1.0	1.0×10 ⁻⁵ – 1.0×10 ⁻¹	28.2	0.9907	8
8	6.0	26.0	-	-	67.0	1.0	1.0×10 ⁻⁶ – 1.0×10 ⁻¹	35.7	0.9993	5
9	7.0	26.0	-	-	66.0	1.0	1.0×10 ⁻⁵ – 1.0×10 ⁻¹	27.9	0.9802	10
10	6.0	25.0	-	-	68.0	1.0	1.0×10 ⁻⁵ – 1.0×10 ⁻²	21.4	0.9280	13
11	6.0	27.0	-	-	66.0	1.0	1.0×10 ⁻⁴ – 1.0×10 ⁻¹	24.5	0.9521	18
12	6.0	26.0	67.0	-	-	1.0	1.0×10 ⁻⁵ – 1.0×10 ⁻¹	19.2	0.9968	23
13	6.0	26.0	-	67.0	-	1.0	1.0×10 ⁻⁵ – 1.0×10 ⁻¹	24.8	0.9881	16
14	6.5	25.5	-	-	67.0	1.0	1.0×10 ⁻⁵ – 1.0×10 ⁻¹	28.6	0.9792	12
15	6.5	26.0	-	-	66.5	1.0	1.0×10 ⁻⁴ – 1.0×10 ⁻¹	24.7	0.9491	14

* NPOE : nitrophenyloctylether ; DOS: Dioctylseccate.

Experimental optimization (Table 1) revealed that DBP provided the most favorable balance between membrane homogeneity, ion mobility, and interaction efficiency with the electroactive material (MIL-101). Sensors plasticized with DBP exhibited the widest linear dynamic range ($1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M), the steepest Nernstian slope (35.7 ± 0.5 mV/decade), the lowest detection limit (1.7×10^{-7} M), and the fastest response time (~ 5 s). In contrast, membranes incorporating NPOE or DOS resulted in significantly reduced sensitivity, narrower

linear ranges, and slower responses, suggesting less efficient ion transport and weaker compatibility between the plasticizer and the MIL-101 framework. The superior performance of DBP can be attributed to its optimal dielectric constant and viscosity, which facilitates efficient partitioning of the Sunset Yellow anions into the membrane phase and ensures rapid ion-exchange equilibrium. Furthermore, DBP's compatibility with both PVC and the MOF ionophore ensured a stable, defect-free membrane structure that prolonged sensor lifetime (14 weeks). Therefore, DBP was selected as the preferred plasticizer, as it enabled the sensor to achieve enhanced sensitivity, reproducibility, and durability compared with NPOE- and DOS-based membranes.

3.2. Potentiometric response of the PVC-membrane sunset yellow selective sensor

Following the completion of optimization studies, the potential response of the PVC-membrane sunset yellow selective sensor was measured against both sunset yellow and other cations. The standard sunset yellow solution and the experimental test solutions of the selected cations were prepared in equal concentration (1.0×10^{-6} - 1.0×10^{-1} molL⁻¹) at pH=7.5. The ionic strengths of all experimental test solutions were adjusted by using sodium nitrate solution (0.1 molL⁻¹) according to the procedure mentioned in our previous study [28-30]. The fabricated PVC-membrane sunset yellow selective sensor was directly immersed into each test solution. When the PVC-membrane sunset yellow selective sensor reached its equilibrium potential in the test solution, the observed potential values were recorded to create potential (mV) – log C (mol/L) graph. As can be seen in Figure 1, the prepared PVC-membrane sunset yellow selective sensor demonstrated a highly selective and sensitive potentiometric behavior to sunset yellow [28-30].

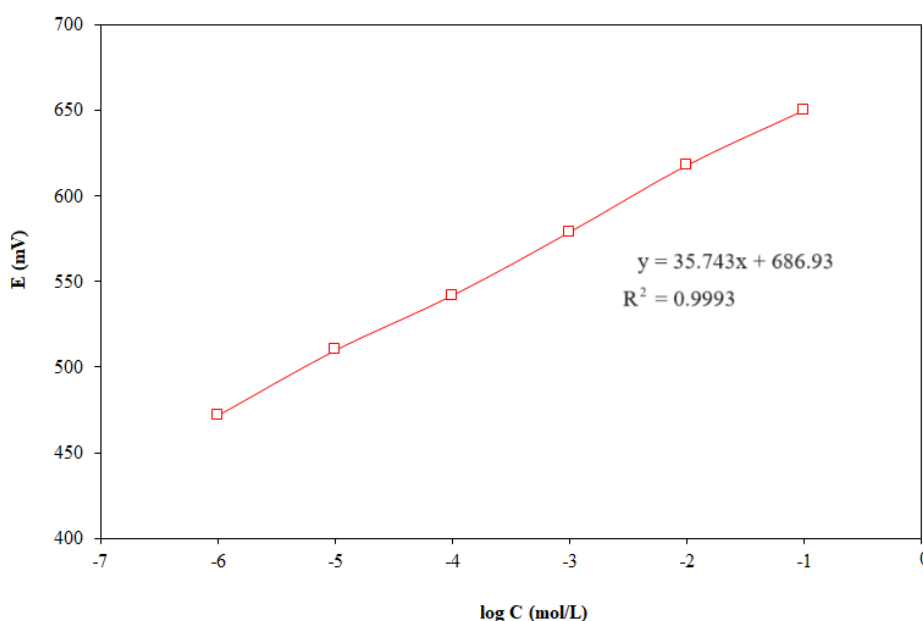


Figure 1. Potential response of the PVC-membrane sunset yellow selective sensor.

3.3. Sensor selectivity

Selectivity is described as the measure of the interference effect of interfering species on the potential response of the sensor and determined by calculating the selectivity coefficient value for each interfering species. In this work, the potentiometric selectivity coefficient values of the PVC-membrane sunset yellow selective sensor were determined with the help of the Separate Solution Method (SSM) which is based on the Nicolsky-Eisenman equation and given as both $K_{A,B}^{\text{pot}}$ and $-\log K_{A,B}^{\text{pot}}$ in Table 2. When the selectivity coefficient values in Table 2 are examined, it can be stated that the developed PVC-membrane sunset yellow selective sensor has exhibited a highly selective potentiometric response. The most interfering ion on the potential response of the sensor was Cd^{2+} . And even in the presence of this ion, the developed PVC-membrane sunset yellow selective sensor exhibited approximately a selective response more than 355-fold for target analyte (sunset yellow) [31, 32].

Table 2. Selectivity coefficients of different interfering ions.

Interfering ion	Separate Solution Method (SSM)	
	$K_{A,B}^{\text{pot}}$	$-\log K_{A,B}^{\text{pot}}$
Cd^{2+}	2.82×10^{-3}	2.55
Ba^{2+}	2.46×10^{-3}	2.61
Ca^{2+}	2.19×10^{-3}	2.66
Mg^{2+}	2.19×10^{-3}	2.66
Fe^{3+}	1.07×10^{-3}	2.97
Ag^{+}	8.91×10^{-4}	3.05
Ni^{2+}	8.71×10^{-4}	3.06
Pb^{2+}	8.32×10^{-4}	3.08
Bi^{3+}	8.32×10^{-4}	3.08
Co^{2+}	7.24×10^{-4}	3.14
Cu^{2+}	7.24×10^{-4}	3.14
Hg^{2+}	6.31×10^{-4}	3.20
Na^{+}	4.68×10^{-4}	3.33
Li^{+}	2.45×10^{-4}	3.61
NH_4^{+}	2.29×10^{-4}	3.64
K^{+}	1.55×10^{-4}	3.81

3.4. pH influence on the sensor response

One of the most important parameters affecting the selectivity and sensitivity of ion-selective sensors is the pH value of test solutions. The pH is defined as the negative logarithm of the activity of hydronium ions dissolved in a solution [33]. Therefore, the effect of hydronium ions on the potential response of the sensor should also be determined. For this purpose, the pH dependence of the developed PVC-membrane sunset yellow selective sensor was tested in the standard solutions containing 1.0×10^{-3} and $1.0 \times 10^{-4} \text{ molL}^{-1}$ sunset yellow. The pH values of the experimental test solutions were changed between 2.5-11.5 and the pH of the solutions was adjusted by using the Tris-HCl buffer system. Results presented in Figure 2 demonstrate that the potential response of the developed PVC-membrane sunset yellow selective sensor is stable between pH=5.40-9.55, and the potential response of the sensor has almost not affected by the change of hydronium ions of the solution in this pH range. The gradually increasing potentials

of the sensor at $\text{pH} < 5.40$ result from the interference effect of hydronium ions present in the experimental test solutions into the sensor matrix. Similarly, after pH values higher than $\text{pH} = 9.55$, the potential response of the sensor begins to decrease rapidly. This decreasing drift in the sensor response is probably associated with the decrease in sunset yellow concentration resulting from sunset yellow complexation with hydroxyl ions in the experimental test solution [26, 27].

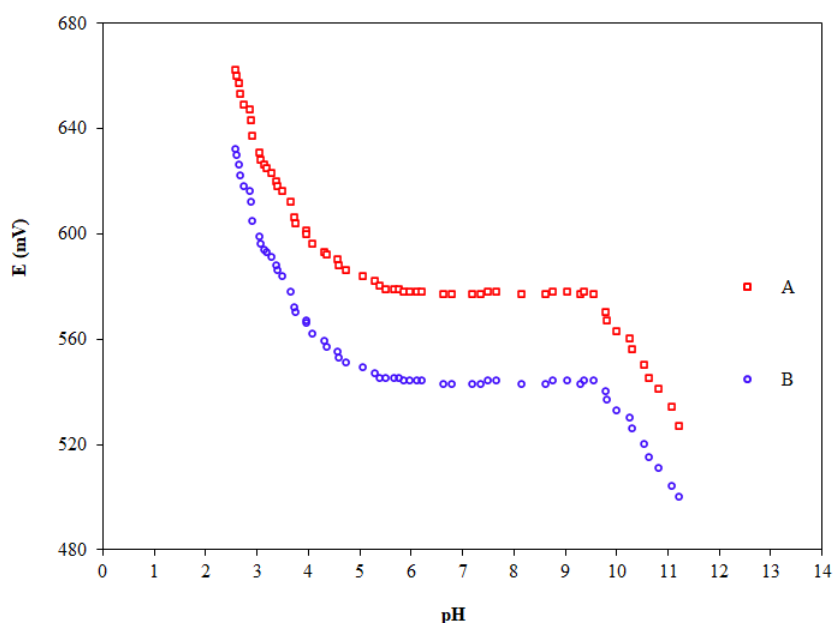


Figure 2. pH influence on the PVC-membrane sunset yellow selective sensor response (A: 1.0×10^{-3} and B: 1.0×10^{-4} molL⁻¹ sunset yellow).

3.5. Response time and repeatability of the sensor

The repeatability of potentiometric sensors refers to the sensor's ability to make the same measurement repeatedly under the same conditions [34]. It is one of the most important performance features that must be realized to observe the accurate and stable performance of the sensor. To quantitatively evaluate the repeatability of the developed PVC-membrane sunset yellow selective sensor, we observed the potential response of the sensor in standard test solutions. For this purpose, the standard test solutions containing 1.0×10^{-3} , 1.0×10^{-4} and 1.0×10^{-5} molL⁻¹ sunset yellow were prepared, and the pH values of these solutions were kept constant at $\text{pH} = 6.0$. The Repeatability measurements were carried out at room temperature and for at least 10 measurements. The obtained repeatability data were demonstrated in figure 3. As seen in Figure 3, the repeatability of the sensor response was very good and the average potential drift of the sensor in tested each concentration range was less than ± 0.5 mV.

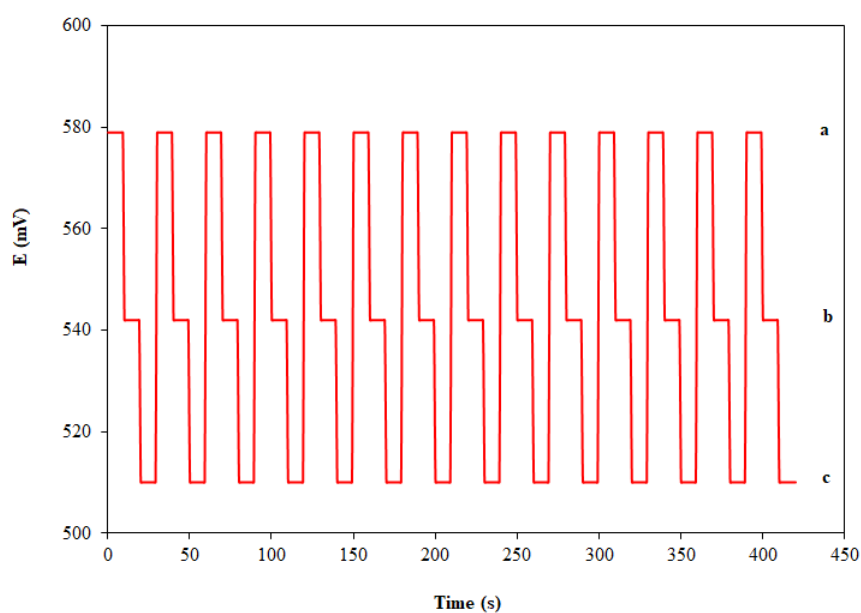


Figure 3. The repeatability of the PVC-membrane sunset yellow selective sensor.

Dynamic response time is a quantitative indicator of the time which takes for the sensor's potential response sensor to reach equilibrium value. It is determined by calculating the average time required to reach 95% of the sensor's equilibrium potential values at low to high or high to low analyte concentrations [35, 36]. In the present study, the dynamic response time of the fabricated PVC-membrane sunset yellow selective sensor was determined by testing 95% of the time it took for the sensor response to reach the equilibrium value when changing from high concentration to low concentration. In the present study, the sensor's dynamic response time was determined by testing the duration time to reach equilibrium potential of the sensor during the transition from high concentration test solution to low concentration test solution. As can be obviously seen from Figure 4, the response time of the developed sensor was quite fast and was calculated as 5 seconds on average.

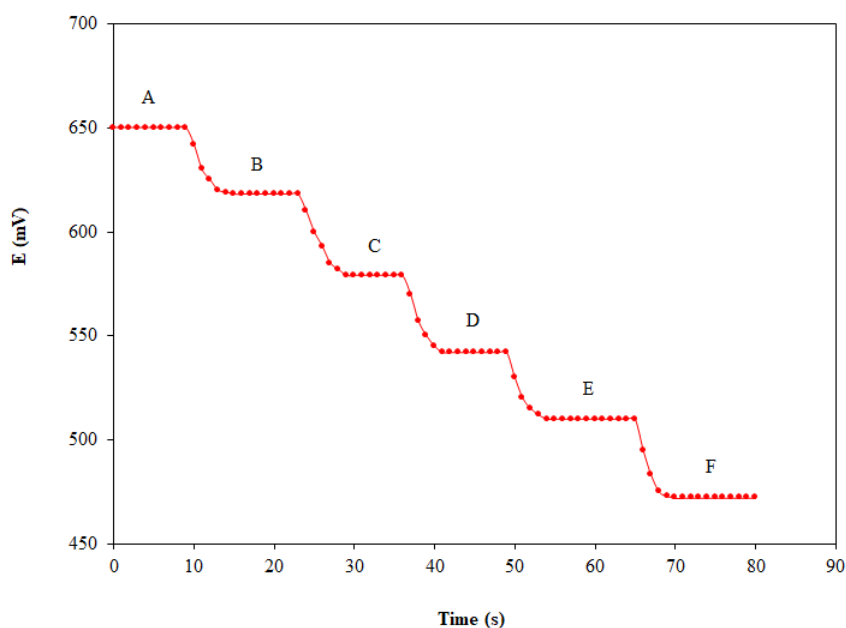


Figure 4. The response time of the PVC-membrane sunset yellow selective sensor (A: 1.0×10^{-1} , B: 1.0×10^{-2} , C: 1.0×10^{-3} , D: 1.0×10^{-4} , E: 1.0×10^{-5} and F: 1.0×10^{-6} molL⁻¹ sunset yellow).

3.6. Lifetime of the sensor

Lifetime describes to the period of duration time which sensor can exhibit the same performance properties under the same conditions and specifies the usable time until sensor performance drops below an acceptable level [37, 38]. In our study, the lifetime of the developed PVC-membrane sunset yellow selective sensor was determined by conducting weekly calibration measurements with the same sensor under identical conditions and by monitoring the slope values of the linear working range exhibited by the sensor in these calibration measurements. Figure 5 showed that the sensor could be used for 14 weeks without any significant change in its potential response. After the 14th week, significant decreases in the sensor potential response occurred. Therefore, the acceptable lifetime of the sensor was determined as 14 weeks.

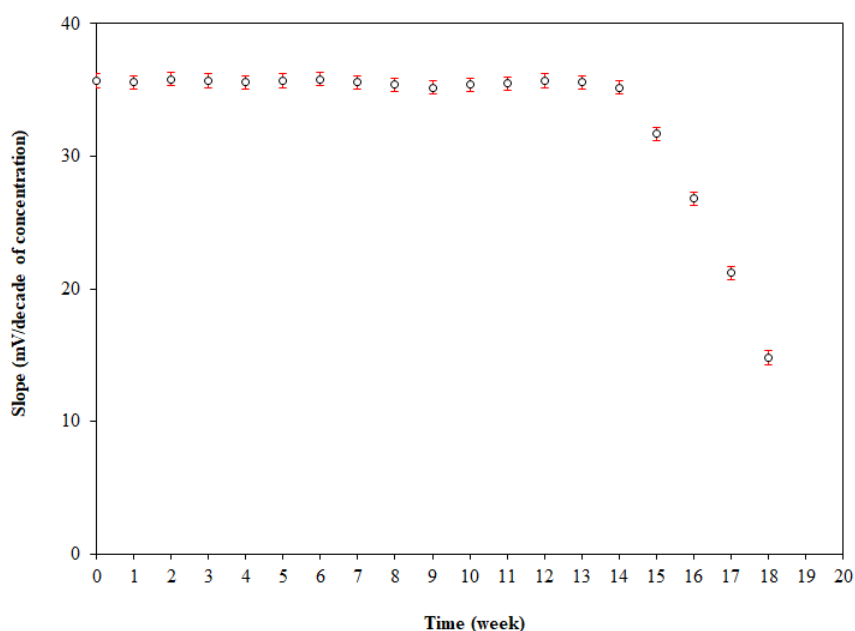


Figure 5. Lifetime of the PVC-membrane sunset yellow selective sensor.

3.7. Comparison of the sensor response characteristics

Comparing sensor performance characteristics with literature is a guided expression that indicates the superior properties of the tested performance characteristics of a developed sensor compared to other similar sensors. In our study, the potentiometric performance characteristics of the developed PVC-membrane sunset yellow selective sensor were compared with similar sensors in the literature. When the data in Table 3 is examined, it is seen that at least one potentiometric performance characteristic of our sensor is superior to a similar sensor in the literature [5, 6, 9, 39, 40].

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

Reference No	Method	Linear range (molL ⁻¹)	Detection limit (molL ⁻¹)	Slope (mV/decade of concentration)	Response time (s)	pH range	Life time (week)
[5]	Voltammetry	1.0×10^{-7} - 2.0×10^{-6}	3.0×10^{-8}	NM	NM	4.0	2
[6]	Potentiometry	1.0×10^{-5} - 5.0×10^{-2}	NM	$23.6 \pm \text{NM}$	~5	6.4-9.1	9
[9]	Voltammetry	0.08-10 (μmol L ⁻¹)	4.2 (nmol L ⁻¹)	NM	NM	2.0-8.0	NM
[39]	Potentiometry	7.94×10^{-5} - 1.0×10^{-2}	-	-32.9 ± 0.821	-	5.0-10.0	-
[40]	Potentiometry	3.16×10^{-7} - 3.16×10^{-3}	3.16×10^{-7}	-29.8 ± 0.2	<10	4.5-9.5	45 (day)
This work	Potentiometry	1.0×10^{-6} - 1.0×10^{-1}	1.7×10^{-7}	35.7 ± 0.5	5	5.40-9.55	14

*NM: Not mentioned.

The 14-week operational lifetime obtained in this study is indeed noteworthy when contextualized with previous reports. For example, reference [6] reported a potentiometric Sunset Yellow sensor with a lifetime of approximately 9 weeks, while reference [40] achieved a stability of only about 45 days. Similarly, some voltametric sensors for Sunset Yellow have been reported with even shorter usable durations, typically not exceeding 2–6 weeks. In contrast, the MOF-based polymeric membrane sensor developed in our work maintained stable performance for 14 weeks without significant potential drift. This extended stability can be attributed to the strong structural compatibility between the MIL-101 ionophore, PVC matrix, and dibutyl phthalate plasticizer, which together ensured membrane homogeneity and long-term operational robustness. Therefore, compared with the lifetimes of similar Sunset Yellow sensors reported in the literature, the present sensor demonstrates superior durability, further highlighting its practical applicability.

3.8. Analytical applications

The usability of the sensor in different analytical applications was tested both in the potentiometric titration of sunset yellow and the direct determination of sunset yellow in different food samples. In potentiometric titration application, a $1.0 \times 10^{-2} \text{ molL}^{-1}$ 30.0 mL sunset yellow solution was titrated with a $1.0 \times 10^{-1} \text{ molL}^{-1}$ silver nitrate solution in Tris HCl buffer solution at pH=7.50. For this purpose, a 0.1 mL of titrant solution was slowly added to $1.0 \times 10^{-2} \text{ molL}^{-1}$ 30.0 mL sunset yellow solution and the observed potentiometric signals were continuously monitored by the PVC-membrane sunset yellow selective sensor (Figure 6). Potentiometric titration application was performed in triplicate using the same sensor and the end point of the potentiometric titration was calculated as $3.1 \pm 0.2 \text{ mL}$. The resulted potentiometric titration application shows that the developed sensor can be used as a fast and reliable alternative analysis method, especially in industrial applications, for the direct determination of Sunset Yellow with high selectivity.

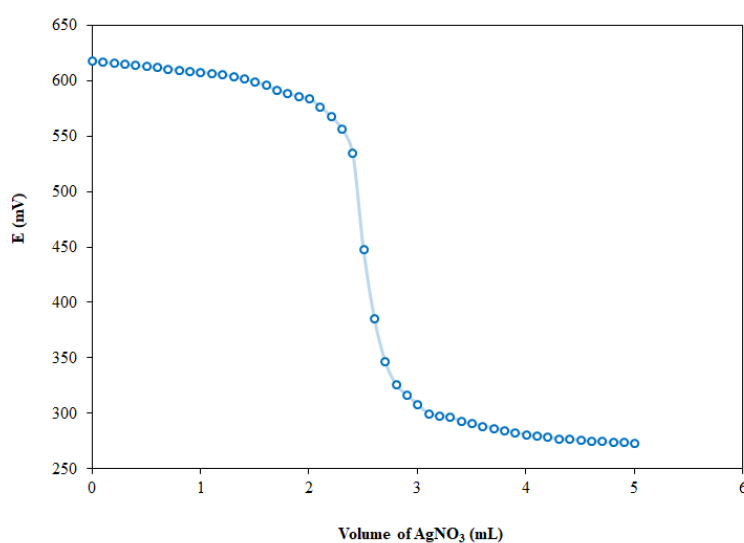


Figure 6. Potentiometric titration of 30 mL of $1.0 \times 10^{-2} \text{ molL}^{-1}$ sunset yellow with 1.0×10^{-1} silver nitrate solution at pH=7.5 using the PVC-membrane sunset yellow selective sensor.

As another analytical application, the sunset yellow content of different pharmaceutical samples such as ZINCO, POLIVIT and CALPOL 6 PLUS and different water samples such as tap water, dam water and lake water were determined by standard addition method with the developed sensor. The preparation of different drug samples containing sunset yellow for potentiometric analysis was carried out according to the procedures expressed in our previous study.

Before the potentiometric measurements, the sensor was calibrated using standard sunset yellow solutions and a calibration curve was created. The amount of sunset yellow in each sample was measured by making five repeated measurements with the PVC-membrane sunset yellow selective sensor. The results obtained were summarized in Table 4. As seen in Table 4, the data obtained with the PVC-membrane sunset yellow selective sensor was consistent with the comparison method at a 95% confidence level. As a result, the developed PVC-membrane sunset yellow selective sensor could be successful in using both analytical applications (potentiometric titration and real drug analysis).

Table 4. Determination of sunset yellow content in different samples and statistical calculations. (*Results are given as mean standard deviation of five replicate analyses for each sample)

Sample	Estimated SY ppm	Added SY ppm	Found SY by Sensor * ppm	Relative error %	Recovery %
Tap water	-	452.40	461.3±1.2	1.97	98.03
Dam water	-	452.40	459.7±1.5	1.61	98.39
Lake water	-	452.40	458.6±1.2	1.30	98.70
ZINCO	-	2262.00	2346.9±2.6	3.75	96.25
POLIVIT	-	2262.00	2339.5±2.1	3.42	96.58
CALPOL 6 PLUS	-	2262.00	2324.6±2.2	2.77	97.23

4. Conclusion

This study presents the design, optimization studies, performance tests and analytical applications of a new sunset yellow selective polymeric membrane sensor containing metal organic framework (MIL-101) material. The developed sensor for highly selective direct determination of Sunset Yellow has demonstrated very satisfactory performance in analytical applications. It has been observed that the metal organic framework (MIL-101) material increases the selectivity of the sensor against sunset yellow and improves its sensitivity. As shown in Table 3, the developed sensor exhibited a remarkably wide linear range of 1.0×10^{-6} – 1.0×10^{-1} M and a low detection limit of 1.7×10^{-7} M. These values are superior to those reported for many sensors in literature. Therefore, the sensor clearly demonstrates advantages in terms of high sensitivity and broad applicability. The average response time of 5 s is significantly

faster compared to similar sensors reported in literature. This feature provides a distinct advantage, particularly for industrial analyses and on-site applications where rapid measurements are critical. The operational lifetime of 14 weeks surpasses that of many previously reported sensors (e.g., 45 days or 9 weeks). This extended durability represents a strong advantage in terms of cost-effectiveness and sustainability for practical applications.

The applicability of the sensor was validated using a limited set of real samples, mainly water and selected pharmaceutical formulations. Future studies should therefore examine its performance in more complex food matrices, such as dairy products, baked goods, and processed foods. Additionally, its selectivity and accuracy should be further assessed in multi-component systems containing a high level of potential interferences. Additionally, This MOF-based approach could be further advanced by integration into portable and miniaturized sensor platforms for on-site monitoring. Modifying the sensor with different MOF materials may also further improve its selectivity and detection limit. Moreover, the integration of this sensor into food safety monitoring systems and environmental analysis frameworks presents promising long-term research perspectives.

Ethics in Publishing

There is no ethical problem in publishing this work.

Author Contributions

Nurcan Kaya: Data Collection and/or Processing, Methodology, Validation, Investigation

Gulşah Saydan Kanberoglu: Conceptualization, Analysis and/or Comment, Methodology, Investigation, Analysis and/or Comment

Cihan Topcu: Literature Review, Methodology, Validation, Investigation, Analysis and/or Comment, Supervision, Writing

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