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Dye-Based Acceptor as a Colorimetric Chemosensor for Determination of Dual Ions, Tin (II) and Citrate Ion in Aqueous/ Dimethyl Sulfoxide Media with Analytical Applications

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Abstract

Bromopyrogallol Red (BPR) dye (Dibromopyrogallolsulfonphthalein), was evaluated as a highly selective colorimetric chemosensor for tin and citrate ion. BPR displayed rapid response, high specificity, visual determination and good selectivity toward tin and citrate ion over other competing cations and anions in DMSO/H_2O (1:1 v/v) media. The sensing mechanism was discussed by UV–Vis, titration, and a comparison study. Over a wide range from 0.4 μmol L^{-1} to 153.8 μmol L^{-1} and 0.02 μmol L^{-1} to 1.08 μmol L^{-1}, a good linear relationship between the absorbance and the concentration of tin and citrate ion was found respectively and the detection limit was estimated to be as low as 0.06 and 0.003 μmol L^{-1} (S/N = 3) for tin and citrate ion. This proposed chemosensor has also been successfully applied for the determination of citrate in real samples which demonstrates its value of practical applications in food and biological systems.

Keywords
Colorimetric Chemosensor; Bomopyrogallol Red Dye; Tin(II) Ion; Citrate Ion.

1. INTRODUCTION

The research on the design and development of colorimetric and fluorescent chemosensors that selectively detect specific analyte gain a burgeoning interest among the analytical and supramolecular chemists owing to their potential applications in the environmental, biological, industrial, and agricultural field [1].

In designing a chemosensor, the widely used fluorophores or chromophores like quinones, coumarin, fluorescein, phthalocyanine, pyrene, anthracene, naphthalene, boron-dipyrromethene (BODIPYs), cyanine dyes, rhodamines and 8-hydroxyquinoline, etc. as signaling unit are linked suitably with an analyte recognition unit and applied for the detection of various ionic, and neutral analytes [2,3]. With the recognition of the target analyte, the signaling unit showed naked-eye detectable color and/or spectral changes that can be used for both qualitative and quantitative detection of the recognized analyte. Anions are ubiquitous and well known to play a tremendous role in various biological, chemical, pharmaceutical, and environmental processes [4]. Therefore, it has emerged as a promising research area to develop fluorescent and colorimetric chemosensors for facile, rapid, sensitive, and real-time detection of analytes. An ideal colorimetric and/or fluorescent chemosensor have to meet two fundamental requirements: firstly, the receptor should have a high affinity towards the target analyte and secondly, the signaling unit should provide a detectable response free from environmental interference upon analyte binding [5, 6]. The designing and synthesis of chemosensors for detecting different analytes with desire properties can be achieved by modifying the signaling unit and/or the binding unit [5–10].

Tin is a toxic metal that can accumulate in the human body. Tin exists in two oxidation states. These are divalent tin Sn(II) and tetravalent tin Sn(IV) [11]. These forms depend on pH. At pH > 2, Sn(II) forms $Sn(OH)_2$, which has low solubility under anoxic conditions whereas Sn(IV) presents in form of Sn(OH)4 under toxic conditions at lower pHs than 8.0 [12]. Tin is widely used for the production of beverage cans in the food industry and as a corrosion protective coating component. However, used tin for packaging of beverage samples dissolves into the beverage samples depending on the quantity of beverage ingested and pH, acidity, the presence of oxidizing reagents, the extent of complexation or adsorption, solubility, time, and temperature. After the removal of the tin-coated, delaminating and leaching of alloying metals into the contents will cause to be enriched with heavy metals within the food material [13].

The concentration of total tin in food with respect to the time could increase after the filling has been processed in canned vegetables and beverages [14]. It was recorded that concentrations of total tin in canned acidic fruit

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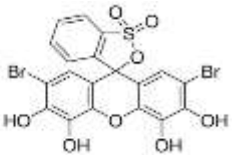
increased depending on the storage conditions [15].

The sensitive, selective, accurate, and precise determination of metals at trace levels is one of the important points of analytical chemistry [16]. Several analytical techniques such as anodic and cathodic stripping voltammetry (ASV and CSV) [17, 18], differential pulse stripping voltammetry (DPSV) [19], inductively coupled plasma-optical emission spectrometry (ICP-OES) [20, 21], inductively coupled plasma-mass spectrometry (ICP-MS) [22], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [23], UV–Vis spectrophotometry [24], electrothermal atomic absorption spectrometry (ET-AAS) [25], spectrofluorimetry [26], graphite furnace atomic absorption spectrometry (GF-AAS) [27] and flame atomic absorption spectrometry (FAAS) [28] were developed to determine tin at trace levels in different samples. Instruments such as ICP-AES and ICP-MS are useful for trace determination without any preconcentration because they are very sensitive to trace/ultra-trace analysis. However, these instruments are more expensive to buy and employ and require expert users. Besides, these techniques have some inherent interferences. FAAS is a comparatively simple instrument, cheap, available in many research laboratories. It is a special feature of high selectivity, specificity, and low susceptibility to matrix interferences.

The design of selective molecular sensors for anions is an area of growing interest due to their important role in a wide range of biological, industrial, and environmental applications [29]. Optical sensors for cation and anions, in which a change in the color or fluorescence intensity is monitored, have been researched extensively for their simple and convenient performance [30]. Moreover, single molecular optical sensors for multiple analytes have become a new research focus because they could allow for simultaneous analysis of multiple analytes, which could overcome the difficulties encountered with loading multiple indicators [31]. One of these anions is the citrate ion. Citrate ion is used for preventing certain types of kidney stones. It is a urinary alkalinizing agent. It works by neutralizing some of the acids in the urine, which helps reduce the formation of crystals. Some of the side effects of citrate ions include severe allergic reactions, black, tarry stools, confusion, severe stomach pain that looks like weakness [32]. Therefore sensitive and selective detection of Citrate ions is essential. Various methods including liquid chromatography [33], capillary electrophoresis, electrochemical, voltammetry [34]. The applications of such methods have been limited due to their wearisome sample preparation, complicated measurement, and low sensitivity.

Ideally, a single molecule, which can sense more than one analytes in different signaling channels could efficiently eliminate interferences, but based on our knowledge, a single molecular sensor that can selectively detect and discern more than one analyte species in different channels has rarely been reported. In addition, the probes reported above were organic and based on synthetic compounds which are rather difficult to synthesize or require expensive instruments for detection. Considering these circumstances, we have undertaken extensive research to explore easily available dyes as high chromogenic and/or fluorescent receptors for cations and anions [35–40]. In this paper, we reported some interesting results of unique colorimetric detection of tin cation and citrate anion by using Bromopyrogallol Red (BPR) dye (Scheme 1) as chemosensor in DMSO/H_2O (1:1 v/v) media. This dye as chemosensor showed high selectivity and sensitivity and fast response and good competition over some other anions and cations. These merits allow the determination of citrate in realistic samples with good recovery.



Scheme 1 The molecular structure of Bromo pyrogallol red [2-(2,7-dibromo-4,5,6-trihydroxy-3-oxo- 3H-xanthen-9-yl)benzenesulphonicacid, BPR] dye.

2. EXPERIMENTAL

2.1. Ragnts

Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without further purification. Bromo pyrogallol red [2-(2,7-dibromo-4,5,6-trihydroxy-3-oxo- 3H-xanthen-9-yl)benzenesulphonicacid, BPR] (Merck) is a dark red crystalline powder with metallic luster; only slightly soluble in water and alcohol and insoluble in nonpolar organic solvents. Solvents used were purified and dried by standard method prior to use. Stock solutions (1.0×10^{-2} mol L^{-1}) of anions were prepared by direct dissolution of proper amounts of potassium salts of SO_3^{2-}, CN^-, F^-, Cl^-, Br^-, I^-, $C_2O_4^{2-}$, $HC_6H_5O_7^{3-}$(Cit^{3-}), CO_3^{2-}, CH_3COO^- (AcO^-), SCN^-, NO_3^-, $H_2PO_4^-$,$C_6H_5COO^-$ (BzO^-), and HSO_4^-ions. Nitrate salts of cations such as Na^+, K^+, Co^{3+} ,Mn^{2+}, Cr^{3+}, Co^{2+} ,Zn^{2+}, Rb^+, Cs^+, Sr^{2+}, Zr(IV),W(VI), Ce^{3+},Mg^{2+},Hg^{2+},Cu^{2+} , TI^+ and Sn^{2+} were purchased from Merck.

Working standards were prepared daily by serial dilutions from the 1.0 $\times10^{-2}$mol L^{-1} concentrated solution. DMSO (Merck) was dried with CaH_2 and then distilled in reduced pressure. BPR was used in DMSO/H_2O (1:1v/v) solution. Solution of BPR with concentration of 5.0×10^{-5} M in DMSO-water was prepared. These solutions were used for all spectroscopic studies after appropriate dilution.

2.2. Istrumntations:

UV-Vis spectra were recorded on a Perkin Elmer Lambda2 and UV- 1601PC Shimadzu Spectrophotometer containing a thermoelectrically temperature controlled cell holder at 298.2 ± 0.1 K in the wavelength range of 300-700 nm with a quartz cuvette (path length =1 cm). Deionized water without any indicator was used in the reference cell. All measurements were made in the absorbance mode. A Hamilton microliter syringe (10µL) was used for titration experiments. A digital pH meter Jenway model 3510 equipped with a combined glass calomel electrode which calibrated against two standard buffer solutions at pH 4.0 and 7.0 was used to measure the pH of the solutions.

2.3. Operating procedures

UV-Vis titration

A solution of BPR (5×10^{-5} mol L^{-1}) was prepared in $DMSO/H_2O$ (1:1 v/v); then 2.5 µL of the solution of this compound was placed in quartz cell (path length=1cm) and changes in the visible spectrum were recorded in $DMSO/H_2O$ (1:1 v/v) solution of this receptor upon addition of 1.0×10^{-2} M of tin cation as its nitrate salt in water solutions. This titration resulted in blue shift in wavelength of maximum absorption from 559 to 549 nm and increased the absorbance intensity in 559nm and decreased the absorbance intensity and removed peak intensity in 436nm (Fig 1). After addition of Sn^{2+}, change color was observed from red to dark violet (Inset Fig 1). After addition of citrate ion to Sn –BPR complex, resulted in blue shift from 549 to 512nm and decreased the absorbance intensity in 549nm and change color was seen from dark violet to pink.

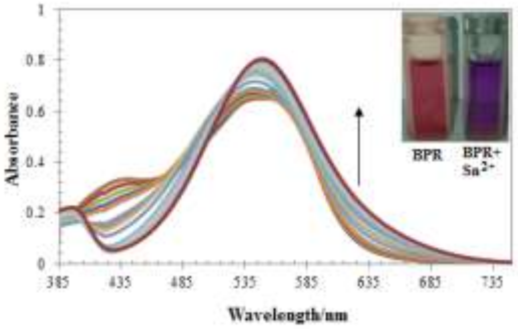


Fig. 1 UV–Vis spectra of BPR (50.0 µmol L^{-1}) upon gradual addition of Sn^{2+} (1.9×10^{-7}–2.5×10^{-4} mol L^{-1}), right inset: corresponding color change of Mure upon addition of 17.3 µmol L^{-1} Sn^{2+} in $DMSO/H_2O$ (1:1v/v).

2.4. Sample preparation

The applicability of the system for real sample analysis is investigated by using different fruit juices. These juices include citrate contents that can be detected. Homogenized samples were prepared by Moulinex. After stirring, the samples were centrifuged at 6000 rpm for 10 min, at 4℃ . The pulp was discarded and after filtering the supernatant through 0.22 µm PTFE filters (Millipore, USA), the sample were diluted to keep the concentration within the calibration range. The samples were kept in amber colored vials and were analyzed immediately after extraction. Standard solutions 1.0×10^{-1} mol L^{-1} of Cit^{3-} were prepared through dissolution of specified amounts of potassium citrate in 100 mL of deionized water. Working standards were prepared daily by serial dilutions from the 1.0×10^{-1} mol L^{-1} concentration. The solutions of potassium citrate salts with known concentrations are used as spiked real samples.

3. RESULT AND DISCUSSION

3.1. The colorimetric and spectral response of probe BPR toward tin

The sensing behavior of BPR with cations was observed by ''naked-eye'' and detection was further confirmed by UV–Vis spectrophotometer. The UV–Vis absorption spectrum of BPR (50 µM) displayed a broad absorption band at 559 nm in $DMSO/H_2O$ (1:1 v/v) media. The binding properties of receptor with Sn^{2+} were studied by UV-Vis titration experiments (Fig. 1). On the gradual addition of Sn^{2+} to a solution of BPR, the absorbance intensity at 559 nm decreased and a blue shift from 559 to 549nm and on isobestic point appeared at 401nm. A change color was also observed from red to dark violet (Inset Fig. 1). The binding behavior of BPR was investigated toward different cations by UV–Vis spectroscopy. Upon the addition of 200 µmol L^{-1} of each cations (Na^+, K^+, Co^{3+} ,Mn^{2+}, Cr^{3+}, Co^{2+} ,Zn^{2+}, Rb^+, Cs^+, Sr^{2+}, Zr^{4+},W^{6+}, Ce^{3+},Mg^{2+}, Hg^{2+},Cu^{2+} , and TI^+), receptor showed little or no spectra changes in absorption peaks (Fig.2).

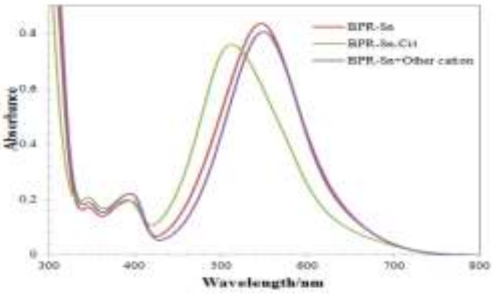


Fig. 2 The UV-Vis absorption changes of BPR (50.0 µmol L^{-1}) in $DMSO/H_2O$ (1:1v/v) toward Sn^{2+} in the presence of cations (Na^+, K^+, Co^{3+} ,Mn^{2+}, Cr^{3+}, Co^{2+} ,Zn^{2+}, Rb^+, Cs^+, Sr^{2+}, Zr^{4+},W^{6+}, Ce^{3+},Mg^{2+}, Hg^{2+},Cu^{2+} , and TI^+) (200.0µmol L^{-1}).

The addition of Sn^{2+} to receptor only caused a significant spectral change and showed immediately a color change from red to dark violet, indicating that receptor can serve as a potential candidate of "naked-eye" chemosensor for Sn^{2+} in $DMSO/H_2O$ (1:1 v/v) solution. These results indicate that BPR could be an excellent chromogenic sensor for Sn^{2+} over competing relevant cations in $DMSO/H_2O$ (1:1v/v) solution. The composition of Sn^{2+} and BPR was estimated by job method. The result in Fig. 3 showed the ratio of tin cation and BPR is 1:1. The association constants with nonlinear fitting analysis by carrying out solver excel was $8.80(\pm 0.19) \times 10^{4} M^{-1}$ (Fig. 4).

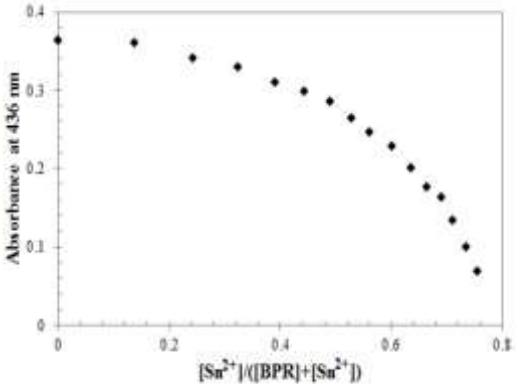


Fig. 3 The stoichiometry analysis of Sn^{2+} complex BPR-Sn^{2+} by job plot analysis of absorbance at 436 nm; versus $[Sn^{2+}]/[BPR]+[Sn^{2+}]$.

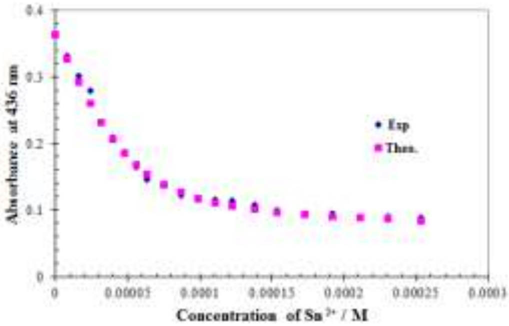


Fig. 4 The Calculation of the association constant (K_{ass}) of [BPR– Sn^{2+}] complex by nonlinear curve fitting using Microsoft excel solver at 436 nm for 1:1 host-guest complexation.

3.2. The colorimetric and spectral response of BPR-Sn complex toward Cit ion

The UV-Vis absorption behavior of BPR-Sn complex in response to various anions was studied and observed color changes from dark violet to pink (Inset Fig. 5) and blue shift from 549 to 512nm upon addition of Cit^{3-} ion to cation-dye complex solution (Fig. 5 and 6) and decreased the absorbance intensity in 549nm.

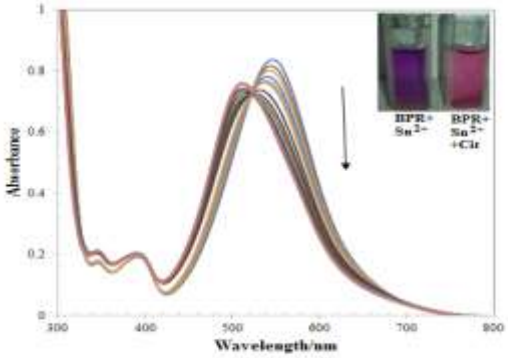


Fig. 5 UV-Vis spectra of BPR (50.0 µmol L^{-1}) with combination of Sn^{2+} (50.0 µmol L^{-1}) upon gradual addition of Cit^{3-} (1.9×10^{-8}–2.7×10^{-5} mol L^{-1})) in DMSO/H_2O (1:1v/v), pH 8.0), right inset: corresponding color change of BPR /Sn^{2+} upon addition of 18.0 µmol L^{-} Cit^{3-} (left to right)) in DMSO/H_2O (1:1v/v).

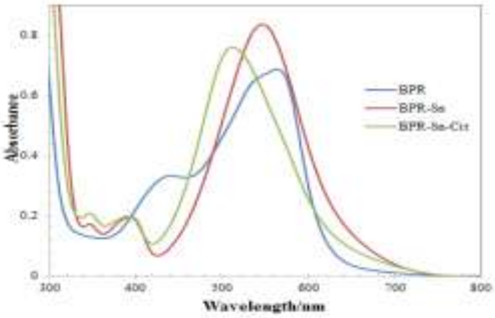


Fig. 6 UV-Vis experiment BPR (50.0 µmol L^{-1}) after the sequential addition of Sn^{2+} (50.0 µmol L^{-1}) and Cit^{3-} (100.0 µ mol L^{-1}) in DMSO/H_2O (1:1v/v).

This behavior was attributed to the interaction of Cit^{3-} ions with BPR-Sn complex. This absorption decrease of complex in response to Cit^{3-} ions was highest with dimethyl sulfoxide (DMSO)/H_2O (1:1v/v) media. It was also observed no change in absorption spectra by adding 300 µmol L^{-1} of various anions (SO_3^{2-}, CN^-, F^-, Cl^-, Br^-, I^-, $(COO)_2^{2}$, CO_3^{2-}, CH_3COO^- (AcO^-), SCN^-, NO_3^-, $H_2PO_4^-$,$C_6H_5COO^-$ (BzO^-), and HSO_4^-ions) (Fig. 7). The 1:1 and 1:2 stoichiometry of the complex (BPR.Sn-Cit) were established by the Benesi-Hildebrand analysis [41] of the absorption titration data.

Table 1. Comparison of analytical features of the previously and recently proposed with present work for the citrate determination.

Sensor	Linear range (µmol L^{-1})	Limit of detection(µmol L^{-1})	Ref.
Colorimetric	0.1-10.0	-	[42]
Colorimetric	0.08-1.6	0.009	[35]
Fluorometric	0.053-0.83	0.006	
Colorimetric	0.17–12.2	0.02	[40]
Colorimetrric and Fluorometric	0.5-0.1	0.18	[43]
Colorimetrric and Fluorometric	0.1-50.0	0.025	[44]
Colorimetric	0.019-1.079	0.003	Present work

When assuming a 1:n stoichiometry for the association between BPR.-Sn complex and Cit^{3-}, the association constant, K_{ass}, is given by the following equation (Eq. (1)):

$$\frac{1}{(A-A_0)} = \frac{1}{(A_{max}-A_0)}\left[\frac{1}{K_{ass}[Cit]^n}+1\right] \qquad (1)$$

A_o is the absorbance of BPR-Sn complex without Cit^{3-}, A is the absorbance of BPR-Sn complex obtained with Cit^{3-}. A_{max} is the saturated absorbance of BPR-Sn complex in the presence of an excess amount of Cit^{3-}; and $[Cit^{3-}]$ is the concentration of Cit^{3-} added. As shown in Fig. 8 and 9, the plot of $1/(A–A_o)$ at 574nm against $1/[Cit^{3-}]$ shows a linear relationship, indicating that BPR-Sn complex associates with Cit^{3-} in a 1:1 and 1:2 stoichiometry (formation of BPR-Sn species) at 549 nm. K_{ass} is determined from the intercept/slope to be $(8.34\pm0.29)\times10^{11}$ mol^{-2} L^{2}.

In Table 1, analytical properties of this method were compared with previous methods [35, 40, 42-44] for citrate determination that indicated this colorimetric chemosensor can detect tin cation and citrate anions with a wide linear and low detection limit.

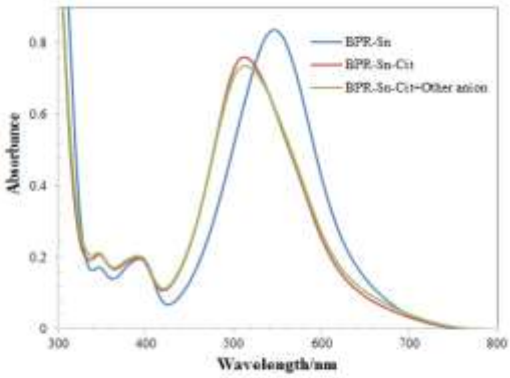


Fig. 7 The UV-Vis absorption changes of BPR/Sn^{2+} in $DMSO/H_2O$ (1:1v/v) toward Cit^{3-} in the presence of anions ((SO_3^{2-}, CN^-, F^-, Cl^-, Br^-, I^-, $(COO)_2^{2}$, CO_3^{2}, CH_3COO^- (AcO^-), SCN^-, NO_3^-, $H_2PO_4^-$,$C_6H_5COO^-$ (BzO^-), and HSO_4^-ions) (300.0μmol L^{-1}).

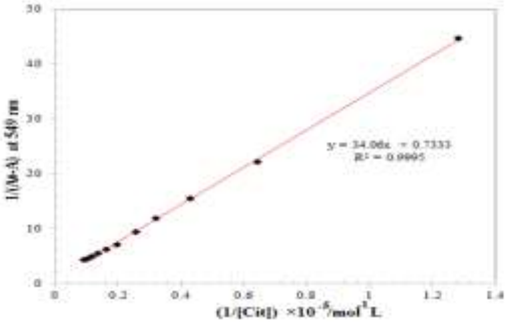


Fig. 8 Benesi-Hildebrand plot of BPR/Sn^{2+} in $DMSO/H_2O$ (1:1v/v) and Cit^{3-} (100.0 μmol L^{-1}), (the variation of $1/(A–A_o)$ at 549 nm versus the function of 1/[Cit]) based on 1:1 binding stoichiometry with Cit^{3-} in $DMSO/H_2O$ (1:1v/v)

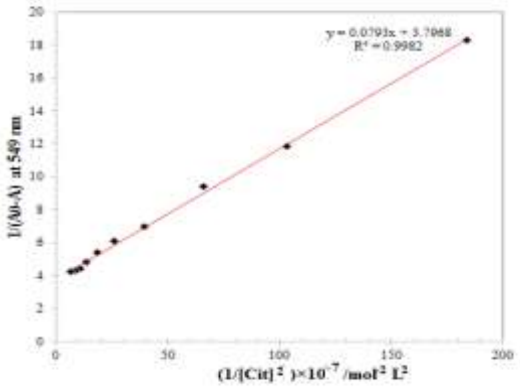


Fig. 9 Benesi-Hildebrand plot of BPR/Sn^{2+} in $DMSO/H_2O$ (1:1v/v) and Cit^{3-} (100.0 μmol L^{-1}), (the variation of $1/(A–A_o)$ at 549 nm versus the function of $1/[Cit]^2$) based on 1:2 binding stoichiometry with Cit^{3-} in $DMSO/H_2O$ (1:1v/v).

3.3. Effect of pH

Sometimes, pH causes color changes with addition of cations and anions, so this interference effect should be studied. Therefore we should find an optimal pH in which chemosensor (BPR) have highest selectivity to detect Sn^{2+} and Cit^{3-} ions .As shown Fig. 10, the absorbance spectra at 559 and 549 nm were obtained over wide pH ranges, 1.5-11.5 by adding tin and citrate ions. Absorption changes differences (A_0-A) in various pH showed that optimal value obtains pH= 5.5. UV-Vis studies were carried out in $DMSO/H_2O$ (1:1v/v) solution.

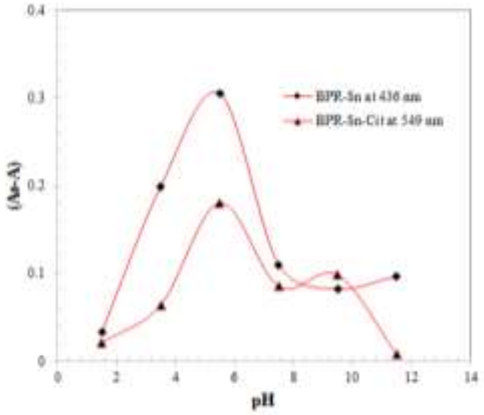


Fig. 10 Effect of the pH on the absorbance changes of BPR (50.0 μmol L^{-1}) in the presence of Sn^{2+} (50.0 μmol L^{-1}) and $[BPR-Sn^{2+}]$ complex in the presence of Cit^{3-} (100.0 μmol L^{-1}) at 436 and 549 nm respectively, in $DMSO/H_2O$ (1:1v/v).

3.4. Fast response

Most chemosensors response with various analyte in long time and slowly. BPR and $[Sn (BPR)]^{2+}$ responses with Sn^{2+} and Cit^{3-} very fast (Fig. 11). Absorption changes and stability were appeared within 1min and 1.0-5.0 min, respectively. The certain optimum values of response time for analytes were less than 60 s. So this sensor is suitable for Cit^{3-} and Sn^{2+} ions.

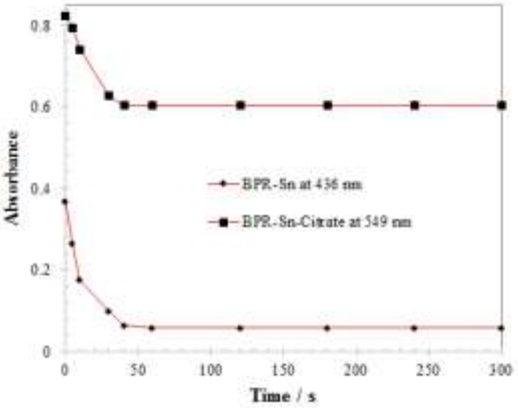


Fig. 11 Response time for the colorimetric detection of Sn^{2+} (50.0 µmol L^{-1}) and Cit^{3-} (100.0 µmol L^{-1}) by BPR and BPR /Sn^{2+} receptors, at 436 and 549 nm, respectively in DMSO/H_2O (1:1v/v).

3.5. *Analytical characterization of Sn^{2+} and Cit^{3-}*

In the optimal experimental conditions, absorbance vs. Sn^{2+} and Cit^{3-} concentration curves were plotted (Fig. 12 and 13).

The linear regression equations were A_{436}=-0.002$C_{Sn^{2+}}$+0.3759 and A_{549}=-0.234 $C_{Cit^{3-}}$+0.8307 with regression coefficients r=0.999. Linear ranges for tin and citrate ions were 0.4 - 153.8 µmol L^{-1} and 0.019-1.079 µmol L^{-1}, respectively. The limit of detection (LOD) was calculated in accordance to the official compendia methods by $3S_b/m$ that S_b and m are standard deviation and the slope of calibration curve, respectively. LOD estimated for Sn^{2+} and Cit^{3-} in DMSO/H_2O (1:1 v/v) were 0.06 µmol L^{-1} and 0.003 µmol L^{-1}. Under the optimal condition, repeatability for tin and citrate ions were measured. RSD %(n=10 $C_{Sn^{2+}}$=3.187 and $C_{Cit^{3-}}$=0.95 µmol L^{-1}) were calculated 1.93% and 2.5% for tin and citrate ions, respectively.

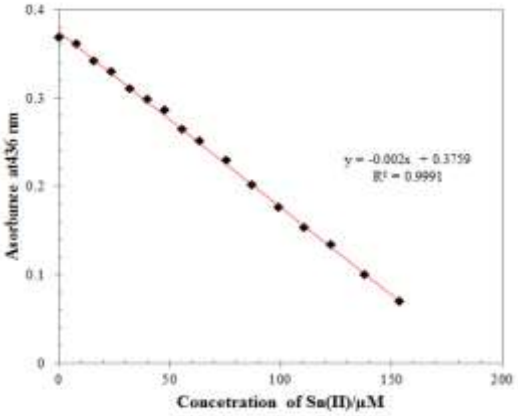


Fig. 12 The linearly proportional relationship between the absorbance of BPR solution at 436 nm and the concentration of Sn^{2+} in DMSO/H_2O (1:1v/v).

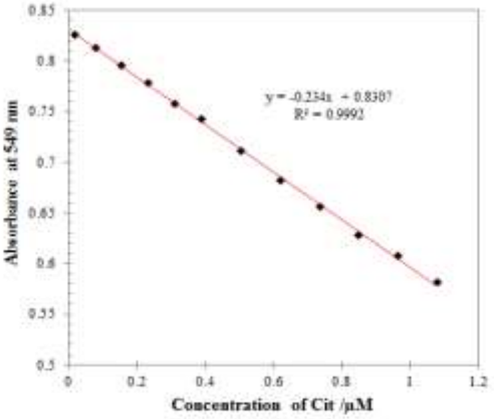


Fig. 13 The linearly proportional relationship between the absorbance of BPR /Sn^{2+}solution at 549 nm and the concentration of Cit^{3-} in DMSO/H_2O (1:1v/v).

3.6. *Analysis of citrate ions in real samples by the present developed assays and commercial enzymatic kit assays*

Six samples from fresh juice of apples, oranges and lemons were analyzed for determining citrate by the current developed procdure. The samples were analyzed by the Biovision Inc. (Mountain View, California) commercial kits for citrate (K655) according to the manufacturer instructions. The proposed method was applied for determination of Cit^{3-} in juice samples. Cit^{3-} content in water samples was determined via the developed colorimetric (A) and commercial enzymatic kit (B) methods (Table 2).

Table 2. Determination of Cit^{3-} some juice samples by proposed method (mean ± standard deviation, n = 6).

Sample	Cit^{3-} (mmol L^{-1}) Proposed method	Cit^{3-} (mmol L^{-1}) Reference method[1]	%R(Added 0.05 mmol L^{-1} Cit^{3-}	Relative error
Orange juice[2]	59.1±1.8	60.3±2.3	97.6	+2.5
Lemon juice[3]	301.3±2.6	298.7±3.1	101.2	-1.4
Apple juice	ND[4]	ND	104.3	-

[1] Commercial enzymatic kits (K655)

[2] Value determined after 10^5 times dilution.

[3] Value determined after 10^6 times dilution.

[4] Not detect.

Good agreement between the percentage recovery determined by the developed colorimetric method, and Commercial enzymatic kits (K655) was achieved and always higher than 95% confidence confirming the precision of the independence of the method from matrix interference. Statistical treatment of data using F test [45] revealed that, no significant differences between the two variances of the developed and commercial enzymatic kits methods. The student t test [45] was also applied to the analytical data of the developed and commercial enzymatic kit methods. No significant difference was observed between the two methods. The tabulated t value at 95% confidence limit was 2.306 and the calculated t value by applying Student's t-test to the results of juice samples were found less than 2.306 for five measurements. The results show that this method is suitable for determination of citrate concentrations in such samples on the other hand the present method is much cheaper in comparison to the enzymatic kits.

4. CONCLUSION

In this paper, Bromopyrogallol Red (BPR) as a new and simple sensor has been used and characterized (UV-Vis spectroscopy). Color changes and spectra changes by naked eye and UV-Vis spectrophotometer were studied by presence of tin and citrate ions in DMSO/H_2O (1:1 v/v). The main advantage of proposed method is simplicity, using of inexpensive instrument, any previous treatment for samples used, and tin and citrate ions determination with very high accuracy, selectivity, fast response and sensitivity and low limit of detection. This sensor can also be applied for tin and citrate determination in real sample.

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پذیرنده بر پایه رنگ به عنوان یک حسگر شیمیایی رنگ سنجی برای تعیین دو یون: قلع (II) و آنیون سیترات در محیط های آبی / دی متیل سولفوکسید با کاربردهای تجزیه ای

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رنگ برومو‌پیروگالول قرمز (BPR) (دی برومو‌پیروگالول سولفو نفتالن)، به عنوان یک حسگر شیمیایی رنگ سنجی بسیار گزینش پذیر برای کاتیون قلع(II) و آنیون سیترات مورد ارزیابی قرار گرفت. پاسخ سریع، عملکرد اختصاصی، تعیین چشمی و گزینش پذیری مناسب برای کاتیون قلع(II) و آنیون سیترات نسبت به سایر کاتیون ها و آنیون های رقیب را در محیط دی متیل سولفوکسید/آب (v/v 1:1) نشان داد. مکانیسم شناسایی این روش به وسیله تکنیک های اسپکتروفتومتری فرابنفش–مرئی، تیتراسیون و یک مطالعه مقایسه ای مورد بحث قرار گرفت. در محدوده خطی وسیعی از ۰/۴ تا ۱۵۳/۸ میکرومول بر لیترو ۰/۰۲ تا ۱/۰۸ میکرومول لیتر با یک رابطه خطی خوب بین جذب و غلظت به ترتیب برای یون های قلع(II) و سیترات بدست آمد. حد تشخیص تخمین زده می شود برای یون قلع(II) و سیترات به ترتیب ۰/۰۶ و ۰/۰۰۳ میکرومول بر لیتر (S/N = 3) اندازه گیری شد. این حسگر شیمیایی پیشنهادی همچنین برای تعیین سیترات در نمونه های حقیقی که ارزش کاربردهای عملی آن را در سیستم های غذایی و بیولوژیکی نشان می دهد، با موفقیت به کار گرفته شد.

واژه‌های کلیدی

حسگر رنگ سنجی شیمیایی؛ برومو‌پیروگالول قرمز؛ یون قلع (II)؛ یون سیترات.