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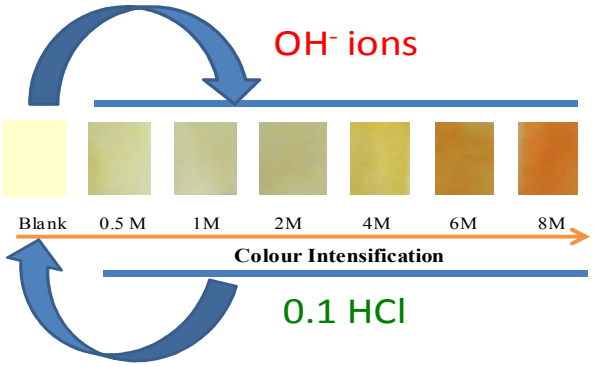
Complete List of Authors:	Thakur, Neha; Bhabha Atomic Research Centre, Analytical Chemistry Division Abhay Kumar, Sanjukta; BARC, Atomic Energy Pandey, Ashok; Bhabha Atomic Research Centre, Radiochemistry Division Kumar, Sangita; Bhabha Atomic Research Centre, Analytical Chemistry Division Reddy, A.; BARC, Analytical Chemistry Division

Graphical Abstract



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ARTICLE

Optode sensor for on-site detection and quantification of hydroxide ions in highly concentrated alkali solutions

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Neha Thakur,[a*] Sanjukta A. kumar,[a] Ashok K. Pandey,[b] Sangita D. Kumar,[a] and A.V.R. Reddy[a]

A colorimetric strip sensor has been developed for selective visual detection and quantification of hydroxide ions in a highly concentrated alkali solutions. The sensor was made by immobilizing the 4,4-bis-[3-(4-nitrophenyl) thiourea] diphenyl ether derivative of thiourea in a Whatman 541 filter paper. Immobilization of the derivative was optimized with respect to its concentration, stability and uniformity in the solid substrate. The sensor strip on reaction with hydroxide ions turns orange in color, and the intensity of the color was found to be proportional to the concentration of hydroxide ions. Developed strip sensor exhibits a wide linear dynamic range of 0.5 M to 8 M and a response time within 5 min. The adequate reproducibility as well as reusability of the strip sensor is suitable for a rapid on-site quantification of hydroxide ions in concentrated alkaline media. The developed strip sensor was successfully applied for the determination of hydroxide concentration in nuclear fuel decladding solutions.

Introduction

Sodium hydroxide is one of the most common raw materials used in various industrial applications. The main uses of concentrated sodium hydroxide globally are in paper pulp, electroplating, alumina and chemical industries as well as in waste water treatment plants.[1-4] Although it is the largest chemical manufactured in the world, it is highly corrosive that necessitates a need to develop on-line monitoring sensors for its determination in the high concentration range.[5-6] The commonly existing methods for measuring hydroxide ion concentration include the electrochemical sensor based pH determination with glass electrode and volumetric titrations. Glass electrode based determinations are précised only in the lower concentration level (pH 2-12).

At hydroxide concentrations above pH =12, the electrochemical sensors become highly unstable and result in large errors.[4,7-8] Titrimetry, Flow injection analysis (FIA), conductivity measurements, thermometric ion-exchange and near-infrared spectroscopy (NIRS) are some of the other methods of measuring sodium hydroxide concentration.[9-12] The standard method of titration suffers from several drawbacks such as requirement of several reagents and long analysis time. The FIA method involves measuring the conductivity of the species and its mobility in the solution. Dependence of the signal on the conductivity of the sample makes it a non-specific method and hence it may suffer from interferences. The thermometric ion exchange measures the thermal transient of the base sample when it is eluted from an ion-exchange bed and is capable of measuring sodium hydroxide concentration up to 5 M but proper sampling of the solution is a major issue associated with this method.[13]

pH paper strips have been widely used for qualitatively measuring the alkalinity of the solution. There are a variety of pH strips available which differ by their sensitivity and the range of pH they are designed for. However, most of these are limited to a particular concentration range and shows a visual color change only upto 0.1M hydroxide ion concentration (pH = 13) beyond which they shows a dark blue color irrespective of the hydroxide concentration. Therefore over the past few years, focus has been to develop sensors for monitoring hydroxide ions in the extremely harsh environments.[14-18] Reagent based fiber - optic sensors have been developed to examine the possibility of on-site analysis of the process and environmental streams without the need of sampling.[19] Recently, the approach of immobilizing dyes in different polymer matrices has been reported for sensing of hydroxide ions or hydrogen ions.[20-22] The principle of sensing hydroxide in these sensors is based on either monitoring of the fluorescence or measuring absorbance changes. However, most of these reported sensors suffer from the degradation of the base matrices when equilibrated with highly concentrated alkaline solutions, and thus they are limited upto pH=13. Beyond this, it is reported that they do not produce measurable optical changes and thus limiting their applicability.[20,23] Recently, an optical sensor based on incorporation of 2-pyridylazo compounds in polystyrene films for the detection of concentrated hydroxide has been reported.[24] But the use of glass slide as a base for forming the sensor film makes it non-reproducible. Therefore, there is a need to develop a simple, sensitive, self-supporting and highly reproducible optical sensor for the measurement of higher concentration of sodium hydroxide.

Recently, paper based sensors are being widely used for fabricating the simple, low-cost, portable and disposable

strips. The analytical devices made using these strips can be integrated in a manner that these are flexible, portable, disposable and easy to operate.[25-27] The unique properties of paper such as high porosity, ease of liquid transport via capillary action and its compatibility with different chemicals are the advantages for using it as a sensing base platform. Recent years have witnessed the development of many filter paper based sensors for the detection of various metal ions.[28-30]

We have developed a filter paper based color changeable optode sensor for measuring hydroxide concentration of highly alkaline media. The sensor strip is made by immobilizing a thiourea derivative namely 4,4-bis-[3-(4-nitrophenyl) thiourea] diphenyl ether in a Whatman 541 filter paper. To the best of our knowledge, this is the first time that this reagent has been explored for the detection and quantification of highly concentrated hydroxide ions in aqueous solution although thiourea derivative containing nitrophenyl group as a signal generating unit has been used as a reagent for the detection of fluoride and cyanide in organic media.[31]

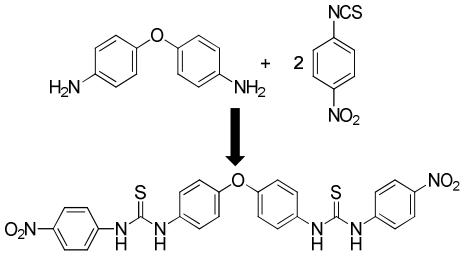
Synthesis of the derivative has been carried out using a one step procedure reported in the literature.[31] Based on the preliminary experiments carried out, it has been observed that Whatman 541 filter paper is the best base matrix for physical immobilization of the derivative. The conditions for the synthesis of optode have been optimized so as to obtain optimum signal response. The tolerance of the synthesized optode sensor towards other ions is studied. The developed optode shows a selective and reproducible response towards hydroxide ions. It has been applied for detecting and quantifying hydroxide ions in real samples in presence of high concentration of interfering ions.

Experimental section

Reagents and Instrumentation

Cellulose triacetate (molecular weight 72,000-74,000, acetyl value = 43.2%), 4,4-diaminophenyl ether, 4-nitrophenyl isothiocyanate and tri-(2-ethylhexyl) phosphate (TEHP) were procured from Sigma-Aldrich (Steinheim, Switzerland). Poly(styrene) (avg M_w = 2,50,000) was procured from Acros Organics, New Jersey, USA. Sodium hydroxide, dichloromethane, 1,4-dioxane and dimethylsulfoxide (DMSO) were obtained from Merck. All these chemicals were used as obtained. Nano pure water measuring 18.2 MΩ cm^{-1} of specific resistance, collected from Elix, Millipore, Merck ultra pure water system was used throughout the experiments. All absorbance measurements were carried out using USB 4000 Spectrophometer (Ocean Optics, Germany) and the spectra of the optodes were recorded in the reflectance mode.

Thiourea derivative was synthesized using a detailed procedure as described by Kumar et al.[31] Briefly, 1.0 g of 4,4-diaminophenyl ether (0.005 mol) was dissolved in 40 mL dry 1,4-dioxane, and 0.01 moles of 4-nitrophenyl isothiocyanate was added to it. This solution was continuously stirred for 5 h at room temperature. The yellow color precipitate was formed which was filtered and washed thoroughly with 1,4-dioxane. The product so obtained was weighed and the yield obtained was found to be 86%. The reaction involved in the synthesis is shown in Scheme 1.



Scheme1. Reaction scheme for the synthesis of 4,4-bis-[3-(4-nitrophenyl) thiourea] diphenyl ether derivative

Characterization

The synthesised derivative was characterised by FTIR studies. The IR spectra were recorded using diamond single reflectance ATR in IR Affinity-1 spectrometer. The samples were analyzed over the range of 400-4000 cm^{-1}, operating at 4 cm^{-1} resolution.

Fabrication of the optode

For the preparation of optode sensor, Whatman 541 filter paper was dipped in a 0.01% thiourea derivative solution in DMSO: dicholoromethane (1:5 V/V). It was air dried and washed with aqueous solution. It was observed that the immobilized derivative leached into the aqueous phase when dipped in 2 M NaOH solution. In order to prevent leaching, 0.001% cellulose triacetate (CTA) dissolved in dichloromethane was added to the thiourea derivative solution before immobilizing it in the filter paper. This was followed by washing with water and air drying of the loaded filter paper. No leaching was observed when CTA was used along with dye during immobilisation. The derivative loaded filter paper was cut into 2x1 cm^2 strips and used for hydroxide determination.

Measurement procedure and optimisation of parameters

For quantitative measurements, the synthesized optode of 2x1 cm^2 size was placed under an optic fibre probe of an optical fibre based spectrophotometer and absorbance was measured. This was treated as a blank reading. Similar measurements were performed after equilibrating the optodes with varying concentrations of sodium hydroxide and measuring the absorbance at λ_{max} = 438.1 nm. To obtain the best measurement conditions for quantification of hydroxide ions, time taken to attain maximum optical signal as well as tolerance of synthesized strip towards others anions were evaluated. Kinetics was carried out by varying the contact time between the optode (2x1 cm^2) and hydroxide solution of 8 M from 50 to 1000 seconds.

Application to real samples

The applicability of the developed strip sensor was tested in alkaline waste water samples collected from waste immobilization plant (WIP), Trombay. Prior to the analysis of

the samples, they were filtered through 0.45 μm filter paper and then were equilibrated with sensor strips of 2x1 cm^2 sizes. The resultant absorbance of the strips was measured.

Results and discussion

Characterization of synthesized derivative

The FTIR spectrum of the synthesized derivative showed sharp bands in the 500-1600 cm^{-1} region, see Fig.1. The band at 1500-1540 cm^{-1} could be assigned to the bending vibrations of C=C of benzene ring whereas band at 1595 cm^{-1} corresponds to the –NH bending vibrations. The bands in the region of 1100 cm^{-1} – 1230 cm^{-1} were assigned to C-N stretching vibrations. The bands at 3041 cm^{-1} and 3285 cm^{-1} are assigned to -NH stretching vibrations whereas sharp band at the lower region of 500 cm^{-1} corresponds to the –C=S stretching of the thiourea derivative.

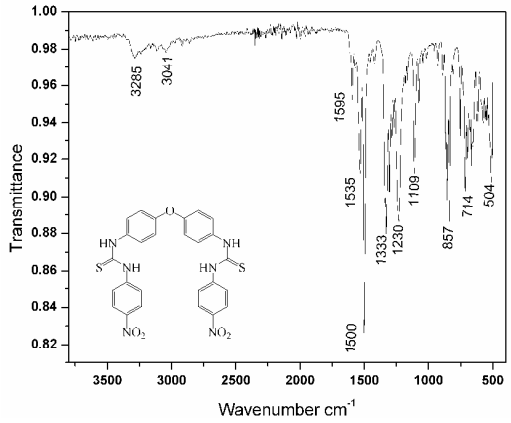
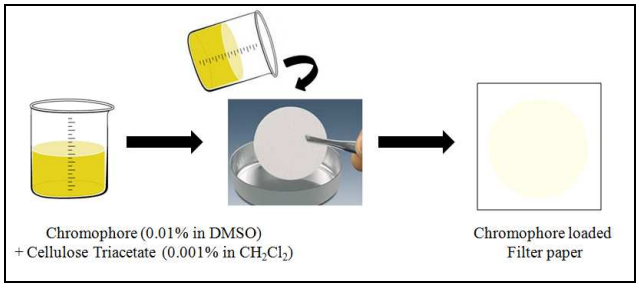


Fig.1 FTIR spectrum of the synthesized (4,4-bis-[3-(4-nitrophenyl) thiourea] diphenyl ether) derivative

Selection of the solid support for synthesis of optode

A support in which synthesized derivative can be immobilized with ease is the choice of the material for fabricating a visual optode sensor. Poly(styrene) was chosen as the base polymer along with the plasticizer tri-(2-thylhexyl) phosphate (TEHP) to form a thin film. For this, 0.1 g of polystyrene in 4 mL CH_2Cl_2 was mixed with 0.1g of TEHP dissolved in 1 mL dichloromethane. To this solution, 0.5 mL of the derivative dissolved in DMSO was added and the mixture was stirred for 20 min. using magnetic stirrer. Resultant solution was poured into a 10.0 cm flat bottom Petri-dish placed horizontally and covered loosely with a lid. After 8 h it was found that DMSO (B.P: 189° C) being less volatile compared to CH_2Cl_2 (39° C) did not evaporate completely and thus the film formed was inhomogeneous. Hence, cellulose triacetate was used as a base support to form the film. The film thus formed was found to be quite inhomogeneous. The poor solubility of synthesized derivative in dichloromethane made it difficult to entrap it in the polymerized film matrices. Therefore, Whatman 541 filter paper was used as the substrate for immobilization of synthesised derivative. Scheme 2 shows the pictorial representation of the steps involved in the formation of visual optode sensor. To prevent the leaching of the derivative back into the solution, CTA was added to the solution of the derivative before entrapping it in the filter paper as explained in experimental section. The solvents were completely evaporated and not trapped in the matrix due to higher porosity provided by the filter paper.



Scheme2. Pictorial representation of the fabrication steps of sensor strip

Performance characteristics of sensor for hydroxide detection

The major requirements for an ideal sensor are its wide linear dynamic range, short response time, selectivity, reusability and long shelf-life. The response of the strip sensor with increasing concentration of hydroxide in the concentration range of 0.5 M to 10 M is shown in Fig. 2.

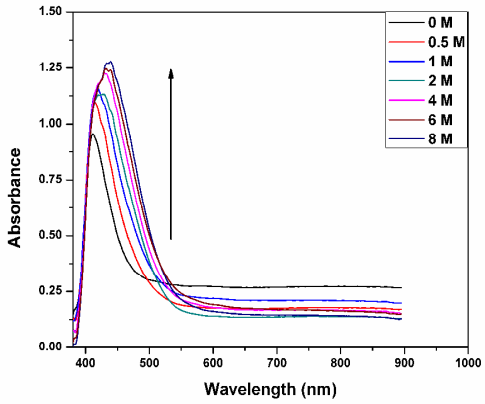
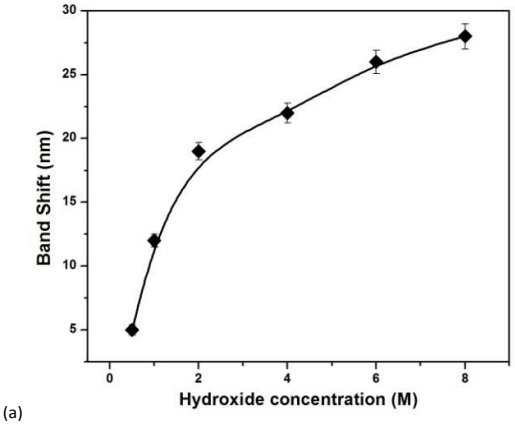


Fig. 2 Absorbance spectra of the sensor strip equilibrated with 0.5 M to 8 M hydroxide solution

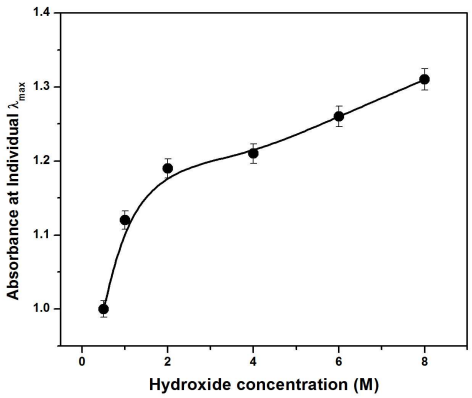
It is seen from the UV-Vis absorbance spectra given in Fig. 2 that the absorbance increases with the increase in the concentration of sodium hydroxide. In addition to that, the increasing concentration of hydroxide ions leads to a slight shift in λ_{max} from 420 nm to 440 nm. The spectral shift obtained in the absorbance spectra , the absorbance at λ_{max}, and absorbance at 438.1 nm of each spectrum were plotted with varying concentration of hydroxide ions (as shown in Fig. 3.

It is seen from Fig. 3a & 3b that band shift and absorbance at λ_{max} did not vary linearly as a function of hydroxide conc. Therefore, the quantification of hydroxide using band shift and absorbance at λ_{max} would require a chemometric method. It is interesting to note from Fig. 3c that the absorbance at 438.1 nm, corresponding to λ_{max} of pristine strip, varied linearly with

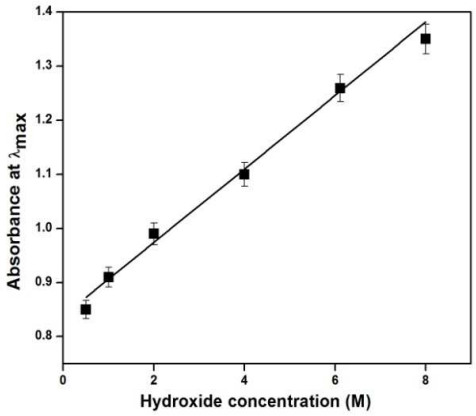
conc. of hydroxide ions. Therefore, for further studies the response of the sensor was measured at 438.1 nm.



(a)



(b)



(c)

Fig. 3 Variations of absorbance at λ_{max} shift (spectral shift) (a) λ_{max} (b), and absorbance at 438.1 nm (c) as a function of hydroxide concentration of from 0.5 M to 8 M

It can be clearly seen that the sensor has a linear response from 0.5-8 M concentration of hydroxide with a linear correlation coefficient (R^2) value of 0.98. Above 8 M absorbance signal was saturated.

The reproducibility in optical response was evaluated by measuring the absorbance change of the optode sensor strips synthesized in different batches for a fixed hydroxide concentration of 6 M. This concentration was chosen as the signal was getting saturated above 8M and our aim is to examine the applicability in higher hydroxide concentration solutions. The relative standard deviation (n=5) obtained in the measurements was 4.5% suggesting a good reproducibility in the sensor response. It was visually observed that the derivative was uniformly immobilized in the optode strip. This was further experimentally confirmed from the absorption spectra of that optode film recorded at six different surface points chosen randomly. The spectra matched well with each other with the variation of absorbance at λ_{max} within 2%.

Response time of any sensor is an important criterion for evaluating its on-site applicability. Typical response curve of the sensor strip as a function of time for a fixed concentration of 8 M hydroxide is shown in Fig. 4. The response time of the developed sensor strip to reach 95% of the maximum response was 5 minutes. However, the response time was higher upto 12 minutes for lower concentration range of 0.5-2 M.

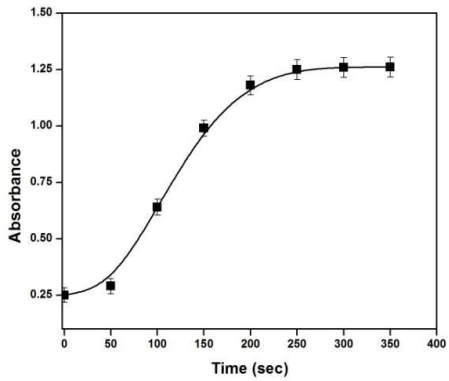


Fig. 4 Absorbance as a function of equilibration time of the sample in 10 mL of 8 M hydroxide solution

The synthesized derivative was used in the colorimetric determination of fluoride and cyanide in organic solution.[31] The idea of employing this derivative for hydroxide sensing arose from the fact that the derivative showed a change in color in alkaline solution even in the absence of cyanide. Hence, the studies were carried for its application for the hydroxide sensing. The preliminary experiments of spectral response of the optode towards other anions; Cl^-, SO_4^{2-}, NO_3^- and PO_4^{3-} were carried out and it was found that they do not produce any spectral response. However, it was important to test the selectivity of the optode sensor in the presence of fluoride and cyanide ions. For this, the optode was equilibrated with 8 M hydroxide solution in the presence of an equimolar solution of fluoride and cyanide ions individually for 300 seconds. After equilibration, the optode was taken out and the absorbance was measured using fibre optic based spectrophotometer (Fig. 5). It was experimentally observed that the absorbance values with both CN^- and F^- ions were comparable to that obtained with a blank optode. However, the response of hydroxide ions was distinct as can be seen from the Fig.5.

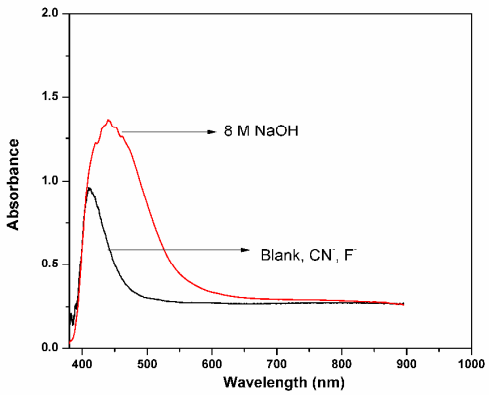


Fig. 5 Absorbance spectra of the optode in the presence of cyanide and fluoride ions (8M) and 8 M hydroxide ions

To explore the possibility of reusability of strip sensor, the hydroxide equilibrated strips were regenerated by dipping it in 0.1 M HNO_3 for 2 min. The cycle of loading hydroxide ions in a strip and regenerating it in 0.1 M HNO_3 was repeated for 12 times. It can be clearly seen from the Fig.6 that absorbance remained nearly constant for first 7 cycles beyond which there was a small but continuous decrease in the absorbance values. The decrease in the absorbance values can be attributed to the degradation of the base matrix on continuous treatment with nitric acid. Therefore the developed sensor can be used upto seven cycles of measurement.

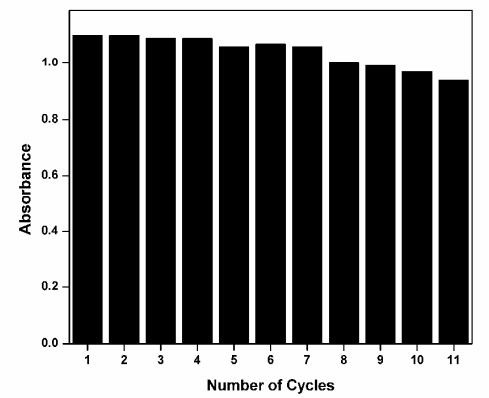
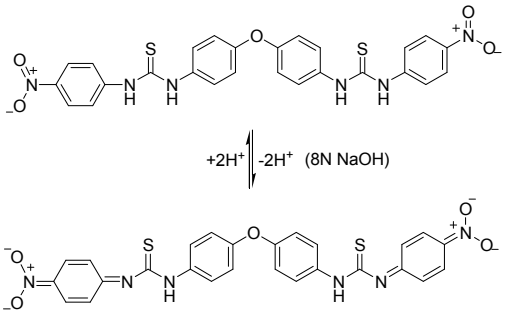


Fig. 6 Absorbance of the same optode strip over 12 cycles of measurement

Sensing mechanism of the sensor

The synthesized derivative exists predominantly in its neutral form RH but in the presence of hydroxide ions it exists in its ionized form R^- resulting in a measurable change in the absorbance.

$$RH + OH^- \longleftrightarrow R^- + H_2O$$



Scheme. 3 Proposed reaction mechanism of the developed sensor

As the concentration of hydroxide ion increases the equilibrium shifts to right and the ratio of $[R^-]/[RH]$ increases. The extended conjugation in R^- shifts the spectra to higher wavelength region resulting in a gradual change of the sensor color from pale yellow to deep orange. The intensity of the color was found to be directly proportional to the concentration of hydroxide ions as shown in the Fig 7 below.

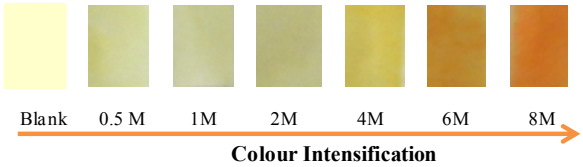


Fig. 7 Change in the color of strip sensor with varying concentration of hydroxide ions

Application to real samples

Sodium hydroxide is used to dissolve the clad of spent nuclear fuel from research reactors. This generates alkaline waste streams. There is a need to measure the hydroxide concentration in such samples. Simulated decladding solutions containing varying concentration of sodium hydroxide were provided by waste immobilization plant (WIP), Trombay. The developed optode sensor was applied to these samples. The composition of a typical sample is given in Table 1.

Table 1. Composition of a typical sample obtained from WIP, Trombay

Elements	Concentration
Fe^{3+}	5 mg L^{-1}
Cr^{3+}	5 mg L^{-1}
Si^{4+}	15 mg L^{-1}
Al^{3+}	10 mg L^{-1}
Carbonate	0.3 M
Sodium Hydroxide	1.5 -4.5 M

Samples were filtered through 0.45 μm filter paper, to remove the suspended particles, if any present, in these samples. Then 2x1 cm^2 of the optode was equilibrated with a sample for 300 seconds and the results obtained are shown in Table 2. Validation of the method was done by the well known titration

method and the results obtained are also shown in Table 2. Both the sets of results are comparable.

Table 2. Analysis of hydroxide in simulated samples collected from WIP, Trombay

Sample	Concentration using optode (M)	Concentration Titrimetry (M)
Sample -1	2.26±0.11	2.56±0.037
Sample -2	3.39±0.15	3.42±0.051
Sample -3	4.7±0.24	4.61±0.072

Conclusions

The present work describes the fabrication of a filter paper based colorimetric strip sensor for the detection of high concentration of hydroxide ions beyond the pH range. The sensor strip was fabricated by incorporating 4,4-bis-[3-(4-nitrophenyl) thiourea] diphenyl ether in a Whatman 451 filter paper. This work demonstrated that the developed sensor can be used to quantify hydroxide ions over a wide range from 0.5 M to 8 M with a relative standard deviation of 4-5%. Equilibration period of 5 min is sufficient for quantitative measurement of hydroxide ions. The sensor reported in the present work is reusable upto seven cycles of measurement. The visual color change of the developed sensor strip with varying concentration of hydroxide ions can provide a simple and convenient method for on-site analysis of concentrated hydroxide. The applicability of the developed optode sensor in real samples was studied by quantifying hydroxide in the process streams generated during decladding of spent fuel from nuclear research reactors.

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Notes and references

[a] *Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India. Fax: +91-22-25505151; Tel: +91-22-25590313; E-mail: thakurn@barc.gov.in.*
[b] *Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India. Fax: +91-22-25505151; Tel: +91-22-25594566; E-mail: ashokk@barc.gov.in.*

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