# Development of UV-cured Polymeric Fluorescence Sensor for Boron Determination

Soner Çubuk*, Mirgül Kosif, Ece Kök Yetimoğlu, Memet Vezir Kahraman

Marmara University, Faculty of Arts and Sciences, Chemistry Department, 34722 Istanbul, Turkey

**Abstract:** This study reports the preparation and characterization of a new polymeric fluorescence sensor for the determination of boron. The sensor was prepared by the UV-curing of glycosyloxyethyl methacrylate (GOEM), 1,6-hexanediol diacrylate (HDDA), 2-hydroxyethylmethacrylate (HEMA), and 2,2′-dimethoxy-2-phenylacetophenone (DMPA) was used as the photoinitiator. The characterictics of the sensor performance including sensitivity, response time, pH effect, stability, and matrix interferences were studied. The excitation and emission wavelengths of the fluorescence sensor were 378 and 423 nm, respectively. With the presented sensor, the optimum pH value for the boron solution was determined as pH 6.0, and the optimum analysis time was selected as 45 seconds. Under the optimized conditions, the linear response range was found to be 9.25 × $10^{-7}$ mol $L^{-1}$ and 9.25 × $10^{-6}$ mol $L^{-1}$. The limit of detection (LOD) was 2.90 × $10^{-8}$ mol $L^{-1}$ and the limit of quantification (LOQ) was 9.66 $10^{-8}$ mol $L^{-1}$ (n=7) with 1.2% relative standard deviation. In addition, boron could be selectively detected by the proposed sensor even in the presence of possible interfering substances. The fluorometric sensor was also successfully applied to real environmental water samples.

**Keywords:** Boron; fluorescence; UV-curing; sensor.

**Cite this:** Cubuk S, Kosif M, Kok Yetimoglu E, Kahraman MV. Development of UV-cured Polymeric Fluorescence Sensor for Boron Determination. JOTCSA. 2017; 4(2): 73-86.

**Submitted:** March 03, 2017. **Revised:** March 10, 2017. **Accepted:** April 10, 2017.

**DOI:** 10.18596/jotcsa.296243.

*Corresponding author: Soner Çubuk. E-mail: sonercubuk@marmara.edu.tr.

## INTRODUCTION

Boron is used in many areas such as defense industry, jet and rocket fuel, soap, detergent, solder, photography, textile dyes, nuclear field, glass fiber, and paper industry. Boron is also necessary for humans and animals as well as being used for different purposes in various industries. This element has a supportive effect on the metabolism such as calcium, magnesium, and vitamin D. However, excessive use for humans can result in eczema, abdominal pain, and nausea (1, 2). In addition, boron is an essential element for plants and its deficiency affects crop productivity and plant growth. The boron content of irrigation waters is very important because it can cause serious damage to some plants when the boron concentration exceeds 1.0 mg $L^{-1}$. According to the World Health Organization (WHO) guidelines for Drinking Water Quality, the amount of boron contained in safe drinking water should not exceed 2.4 mg $L^{-1}$ (3, 4).

The development of methods for the determining of low levels of boron used in various fields is an important issue. For this purpose, numerous methods have been reported such as spectrophotometry (5-8), spectrofluorimetry (9,10), flame atomic emission spectrophotometry (FAES) (11), voltammetry (12, 13), potentiometry (14), ion chromatography (IC) (15) and direct current plasma optical emission spectrometry (DCP-OES) (16). Some of these methods have been described in concentrated sulfuric acid and others have included the solvent extraction procedure. The necessity of carrying out experiments in the concentrated sulfuric acid medium is an important problem. In addition, some of these methods require a long period of time to complete the reaction, or preheating. There is also the interferences of foreign ions among the handicaps of these methods. Another problem is that these methods involve sophisticated instrumentation and complex data collection and processing procedures that require trained personnel. Therefore they are expensive methods and their application areas are limited.

In our study, GOEM-based polymeric fluorescent sensor has been prepared and applied for the detection of trace amounts of boron in environmental water samples. The performance parameters such as response time, pH effect, reproducibility, working linear range, LOD and LOQ were also investigated. The determination of the boron concentration in the real water samples was successfully conducted using the developed sensor.

## MATERIALS AND METHODS

### Reagents and instruments

Glycosyloxyethyl methacrylate (GOEM), 1,6-hexanediol diacrylate (HDDA), 2-hydroxyethylmethacrylate (HEMA) and a photo initiator, namely 2,2'-dimethoxy-2-phenylacetophenone (DMPA) and all other chemicals were supplied from Sigma and used without pretreatment. All experiments performed at room temperature 25 °C with a totally purified water source produced by using a Milli Q-water purification system (Millipore, Labor Teknik-Turkey). The specific resistivity of obtained pure water was recorded as 18.2 MΩcm. A digital pH meter (WTW pH7110) which was continuously calibrated with standard Merck buffer solutions was used to measure pH values of standard solutions. The functional groups in the prepared polymeric membrane were determined by Perkin-Elmer Spectrum 100 attenuated total reflectance-fourier transform infrared spectrophotometer (ATR-FTIR) at 4000-400 $cm^{-1}$. In addition, a Philips XL30 ESEM-FEG / EDAX scanning electron microscope (SEM) was used to investigate the surface morphology of the membrane. Fluorescence measurements were conducted by using a Varian Cary Eclipse spectrofluorometer fitted with a Xenon light source. The slit widths of both excitation and emission bands were set at 5 nm. Perkin Elmer Optima 8300 inductively coupled plasma optical emission spectrometry (ICP-OES) was used to compare the boron concentrations of the real samples with those acquired with the prepared sensor.

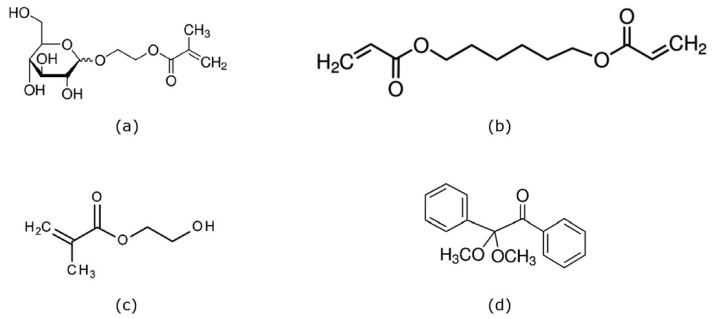


**Figure 1**: Representation of monomers and cross-linker structures of polymeric membrane. a) GOEM, b) HDDA, c) HEMA, d) DMPA.

### Preparation method of fluorescent sensor

The polymeric sensor was prepared by the free radical polymerization of GOEM, HEMA, and HDDA where the latter was used as a crosslinker. Membrane films obtained after the

preparation process can exhibit a number of undesirable conditions such as not uniformly drying, twisting, very rapid swelling in aqueous media or late interaction with aqueous solution as it is excessively hydrophilic, dispersion in water or at different pH. In such cases, reactive monomer, cross-linking monomers and photoinitiator ratios, and curing time under UV light are changed to produce polymeric membranes at desired properties. The optimum monomer and photoinitiator quantities were decided by considering these criteria. A liquid mixture consisting of 63% HDDA, 32% HEMA, 5% GOEM and 3% of total formulation DMPA was stirred well and then poured into specially designed mold (W(cm) x L(cm) x D(cm) =1.2x4.0x2.0). Finally, the formulations were irradiated for 200 s under high-pressure UV lamp (OSRAM 300 W, $\lambda_{max}$ = 365 nm). Then, the membranes were soaked into plenty of deionized water for 12 hours to remove any unreacted residues. At the final step, the membranes were let dry in a vacuum oven at 30 °C to reach a constant weight.

## RESULTS AND DISCUSSION

As it can be seen from the FTIR spectrum (Figure 2), the peak at 3440 $cm^{-1}$ indicates the hydroxyl group of HEMA and GOEM, the strong peak at 1720 $cm^{-1}$ shows the C=O stretching vibration of HEMA. Asymmetric -$CH_2$- stretching was observed at 2936 $cm^{-1}$. The symmetric C-H vibration was found at 2865 $cm^{-1}$ and the asymmetric C-O-C stretching was at 1157 $cm^{-1}$. The peaks at 1407 $cm^{-1}$ and 1071 $cm^{-1}$ were represented CHOO- and C-O vibrations, respectively (12).

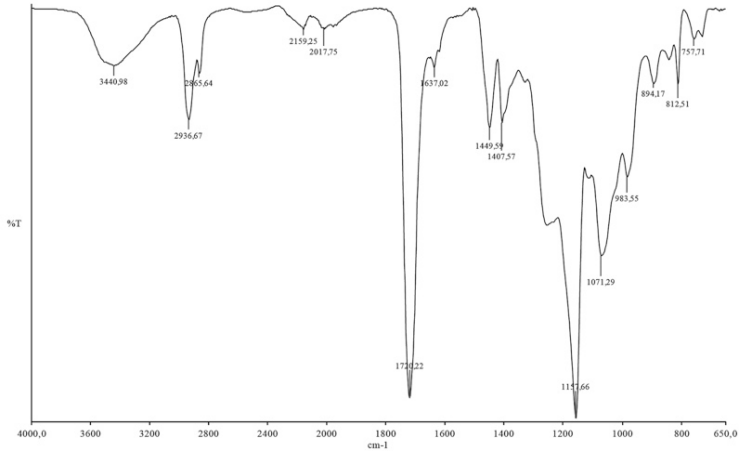


**Figure 2:** FTIR spectrum of boron-sensing polymeric membrane.

The surface area should be homogeneous and non-porous in order that a polymeric film can be useful as a fluorescent sensor. The Figure 3 shows the SEM image results of the boron sensing membrane. The surface of the membrane was scanned at 2500x and 10000x magnification factors for its morphological features. As seen from the SEM images, the membrane surface stands crack-free and expectedly displays a satisfactory homogenous and non-porous surface.

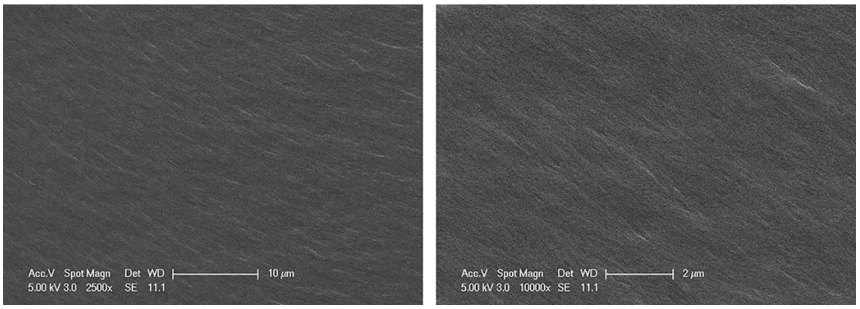


**Figure 3:** SEM images of polymeric membrane at different magnification levels (left: 2500x, right: 10000x).

**Spectral characterization results**

The changes in the fluorescence intensity in the presence and absence of boron were measured by wavelength scanning. The excitation and emission wavelength maxima were recorded 378 nm and 423 nm, respectively (Figure 4).

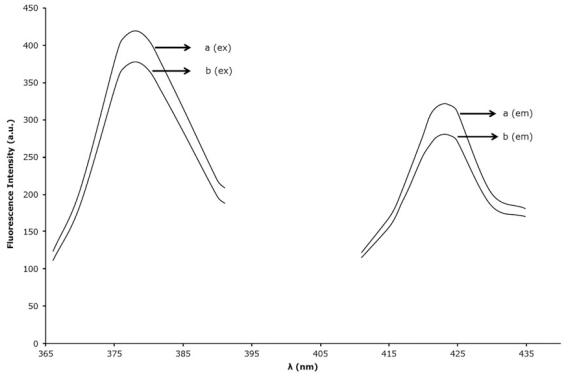


**Figure 4:** The excitation and emission spectra including changes in the fluorescence intensity of the membrane in the absence (a) and presence (b) of $2.31\times10^{-6}$ mol $L^{-1}$ boron ($\lambda_{ex}$= 378 nm, $\lambda_{em}$= 423 nm).

**The study of optimal pH value**

The measurements of fluorescence intensity of the developed sensor were made between the pH range of 1.0–8.0 and within the presence of $2.31\times10^{-6}$ mol $L^{-1}$ boron solution. Buffer solutions were used to adjust the pH value of the medium. In solutions with a pH greater than 8, studies were not conducted because the membrane swelled rapidly and degraded. The membrane was designed to contain GOEM reactive monomer so that it could form a chelate with the boron. Hydroxyl groups and carbonyl groups in the polymeric structure are expected to chelate to boron. Boron complexes are stable in neutral and slightly basic solutions. In this work, as the hydroxyl groups in the polymeric structure are in the *trans* configuration, the formation of the neutral boron ester seems to be favorable, which can also be seen in the literature. Furthermore, tetra-coordinated anionic chelate formation might also be possible by incorporation by hydroxyl and carbonyl groups in the polymeric structure at pH: 6. In addition, it is considered that the fluorescence intensity decreases due to the borate complex in anionic form, which is present at a pH greater than pH 6. The results were shown in Figure 5. It can be seen that the fluorescence intensity notably increased in the range of pH 1.0 to 6.0 by giving the maximum intensity peak at pH 6.0. When the pH is higher than 6.0, it started to decrease. Therefore, pH 6.0 was selected as the optimum pH and this value was used in further experiments.

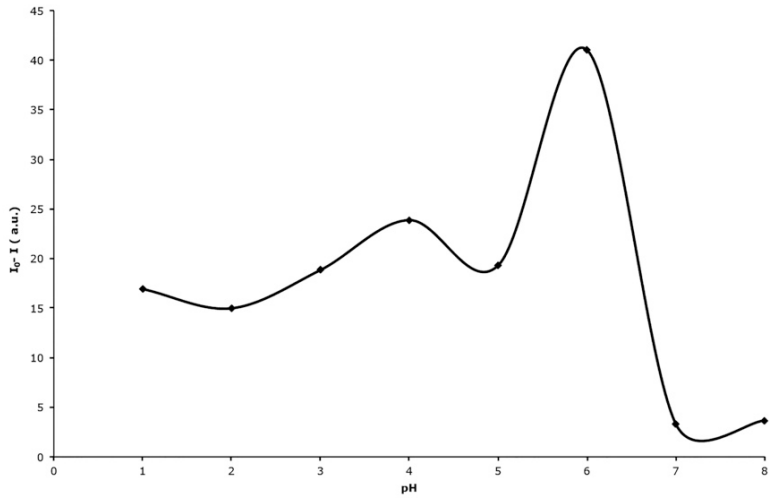


**Figure 5:** Changes in fluorescence intensity with increasing pH values ($I_0$ and I show fluorescence intensities before and after $2.31\times10^{-6}$ mol $L^{-1}$ boron addition, respectively).

**Effect of response time on the fluorescence intensity**

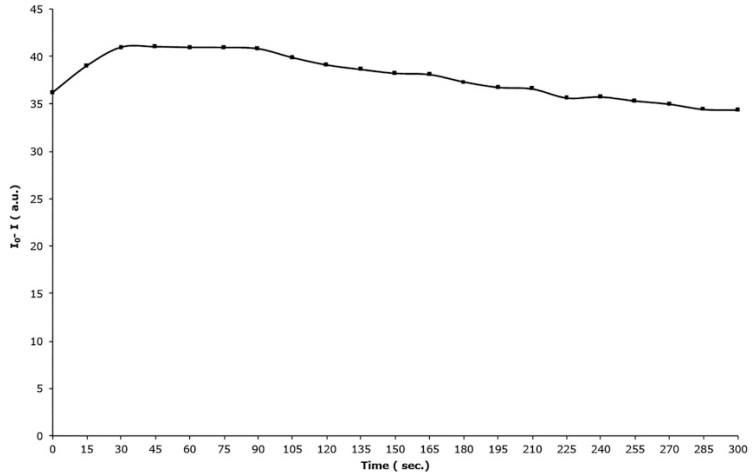


**Figure 6:** Changes of fluorescence intensity of the sensor as a function of time (C= $2.31\times10^{-6}$ mol $L^{-1}$ boron; ($I_0$-I) is found by subtracting the fluorescence intensities measured in the absence of boron (I) from those obtained in the presence of boron ($I_0$)).

Figure 6 indicates the time-dependent changes in the fluorescence intensity of the membrane at pH 6.0. The measurements were carried out for 300 seconds at a time interval of 15 seconds in the presence of $2.31\times10^{-6}$ mol $L^{-1}$ boron. As a result, it was observed that the fluorescence intensity of the membrane increased for 30 seconds, remained constant for 60 seconds and then tended to decrease. For this reason, the optimal response time was chosen to be 45 seconds and this value was used in all other experiments.

**Measurement range, LOD and LOQ**

The calibration graph is plotted as a function of the logarithm of the boron concentration versus the fluorescence intensities under optimum conditions (Figure 7). The fluorescence intensities of boron solutions at different concentrations were measured and the linear relationship between concentration and fluorescence intensity was found between $9.25\times10^{-7}$ mol $L^{-1}$ and $9.25\times10^{-6}$ mol $L^{-1}$. Fluorescence intensities in the absence and presence of boron are indicated by the symbols $I_0$ and I, respectively. LOD and LOQ were calculated as $2.90\times10^{-8}$ mol $L^{-1}$ and $9.66\ 10^{-8}$ mol $L^{-1}$ respectively (n=7).

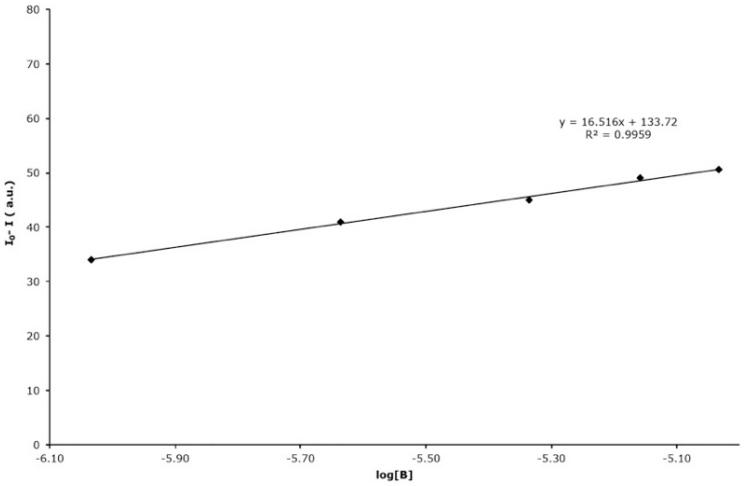


**Figure 7:** Calibration curve obtained under optimal experimental conditions.

**Reproducibility, reversibility, and stability of the sensor**

In the regeneration process, it was observed that the sensor in contact with $2.31\times10^{-6}$ mol $L^{-1}$ of boron solution was able to give initial fluorescence intensities after a wash of only about 40 seconds with distilled water. Thus, the prepared sensor was found to be fully reversible. Reuse of the reagent is not possible, because some of the methods given in the literature are based on the formation of a colored product by complex formation. In addition, disposable electrodes are also used in some of these methods, so it is not possible to reuse the same electrode. However, it was also found that the same sensor can be used 565 times by using the regeneration method proposed in this work. Moreover, the same sensor remained stable for 720 days without any change in structure and its fluorescence intensity.

**Analyses of boron in natural water samples**

The boron contents in drinking water, natural ground water, and standard irrigation were determined by the proposed method. All samples were used directly without any pretreatment. The comparison of the boron concentrations of the samples obtained by ICP-OES and developed method is given in Table 1. The results of developed method and ICP-OES were checked by t-test for accuracy of the presented method. For comparison the t-test (at 95% confidence level) was used but no significant difference between both developed method and ICP-OES was found. According to the results, the proposed sensor could be used safely in determining the boron content in the environmental water samples.

**Table 1:** Results of analysis of boron concentrations in real water samples by the developed method and ICP-OES (95% confidence levels, n=6).

| Samples | *This work (mol $L^{-1}$) | *ICP-OES (mol $L^{-1}$) | RSD (%) | Recovery (%) |
|---|---|---|---|---|
| Drinking water | (3.38±0.04) x$10^{-6}$ | (3.35±0.02) x$10^{-6}$ | 1.16 | 100.24 |
| Irrigation water | (1.91±0.06) x$10^{-6}$ | (1.89±0.04) x$10^{-6}$ | 1.13 | 101.12 |
| Ground water | (2.02±0.03) x$10^{-6}$ | (2.00±0.02) x$10^{-6}$ | 1.17 | 101.18 |

*: The obtained values were expressed as $\bar{x} \pm \frac{t.s}{\sqrt{N}}$

**The influence of some common coexisting ions**

The boron solution at a concentration of 2.31x$10^{-6}$ mol $L^{-1}$ was used to demonstrate the selectivity of the sensor to boron. The foreign ion solutions in different concentrations were added to this solution to monitor how much the fluorescence intensity changed. Table 2 contains the tolerable limit concentrations of the foreign ions. As it can be seen from the table, it is obvious that the developed sensor is highly selective. The potential foreign ions including the strongly interfering ions such as $Fe^{3+}$, $Zn^{2+}$ and $Cu^{2+}$ had no significant effect on the fluorescence intensity of the sensor.

**Table 2:** Tolerance limit concentration of foreign ions (C=2.31×$10^{-6}$ mol $L^{-1}$).

| **Foreign ions** | **Tolerance levels (mol $L^{-1}$)** * |
|---|---|
| $Pb^{2+}$ | 3.62 $10^{-4}$ |
| $Ni^{2+}$ | 8.52 $10^{-4}$ |
| $Ag^{+}$ | 4.63 $10^{-4}$ |
| $Fe^{3+}$ | 1.79 $10^{-3}$ |
| $Cr^{3+}$ | 2.40 $10^{-3}$ |
| $Mn^{2+}$ | 9.09 $10^{-4}$ |
| $Cu^{2+}$ | 1.57 $10^{-3}$ |
| $Co^{2+}$ | 8.49 $10^{-4}$ |
| $Ca^{2+}$ | 2.50 $10^{-3}$ |
| $Mg^{2+}$ | 5.21 $10^{-3}$ |
| $Cd^{2+}$ | 4.45 $10^{-4}$ |
| $Sb^{3+}$ | 3.08 $10^{-4}$ |
| $Hg^{2+}$ | 1.25 $10^{-4}$ |
| $Zn^{2+}$ | 1.34 $10^{-3}$ |
| $Al^{3+}$ | 2.78 $10^{-3}$ |
| $Na^{+}$ | 2.17 $10^{-3}$ |

* Less than ±5% relative error.

**Comparison of some analytical methods with the proposed sensor method**

The comparison of the developed method with several methods and some important parameters are summarized in Table 3. Some of these methods are either performed using a concentrated acid solution or involve an extraction process or require a long analysis time. They are also influenced by the interference of many foreign ions. The developed method is carried out with pH 6 acetate buffer instead of a corrosive medium such as sulfuric acid. Moreover, it did not involve any extraction step and did not cause loss of the analyte.

It is obvious from Table 3, the new polymeric sensor, when compared to the previous techniques, has the lowest detection limit, $2.87 \times 10^{-8}$ mol $L^{-1}$. In addition, the prepared sensor exhibits a high selectivity even in the presence of many foreign ions without the need to use a masking solution. Furthermore, the new polymeric sensor has a minimum response time (45 seconds) and stability up to 720 days compared to the methods in Table 3.

**Table 3:** Comparison with some methods for boron determination.

| Reference | Reagent | Method | Linear range (mol $L^{-1}$) | pH or Medium | Response time | LOD (mol $L^{-1}$) |
|---|---|---|---|---|---|---|
| 5 | 4-methoxy-azomethine-H | Spectrophotometry | 0- $1.3x10^{-4}$ | pH: 5.7 | NM | $4.90x10^{-7}$ |
| 6 | 2,2,4-Trimethyl-1,3-Pentanediol+Carminic Acid | Spectrophotometry | $7.40x10^{-7}$- $1.85x10^{-6}$ | Chloroform | 3 hour | $2.76x10^{-7}$ |
| 7 | Victoria Blue 4R | Spectrophotometry | $2.78x10^{-6}$-$5.09x10^{-5}$ | pH: 2-5 | 30 min. | $1.85x10^{-6}$ |
| 8 | Curcumine- oxalic acid | Spectrophotometry | 0-$3.7x10^{-5}$ | HCl/ ethanol | 1 hour | $7.40x10^{-7}$ |
| 8 | Carminic acid | Spectrophotometry | $6.17x10^{-6}$- $6.17x10^{-5}$ | $H_2SO_4$ | 1 hour | $6.17x10^{-6}$ |
| 9 | Dibenzoylmethane | Spectrofluorimetry | $5x10^{-8}$ - $6x10^{-7}$ | Ether-Conc. $H_2SO_4$ | 60 min. | $4.62x10^{-8}$ |
| 10 | Alizarin Red-S | Spectrofluorimetry | $2.31x10^{-6}$- $9.25x10^{-5}$ | pH 7.4 | NM | $6.66x10^{-7}$ |
| 11 | Methanol | FAES | $9.25x10^{-4}$- $1.85x10^{-2}$ | 60% $H_2SO_4$ | 60 sec. | $2.74x10^{-4}$ |
| 12 | Alizarin Red S | Voltammetry | 0- $1.48x10^{-5}$ | 7.5 | 5 min. | $1.48x10^{-6}$ |
| 13 | Tiron | Voltammetry | $2.59x10^{-5}$- $1.11x10^{-3}$ | 7.5 | NM | $7.77x10^{-6}$ |
| 14 | NaF | Potentiometry | $9.25x10^{-5}$-$4.63x10^{-2}$ | pH:1 | 20 min. | NM |
| 15 | %10 HF | IC | $4.63x10^{-6}$-$4.63x10^{-2}$ | 1 M NaOH | 10 min. | $4.63x10^{-6}$ |
| 16 | NM | DCP-OES | 0-$4.62x10^{-5}$ | MIBK/ glacial $CH_3COOH$ | NM | $1.94x10^{-6}$ |
| This work | GOEM | Spectrofluorimetry | $9.25x\ 10^{-7}$- $9.25x10^{-6}$ | pH:6 | 45 sec. | $2.87x10^{-8}$ |

NM: Not mentioned

## CONCLUSION

In this study, a rapid and selective fluorescence polymeric sensor was developed for boron determination in environmental water samples. The developed sensor does not include the disadvantages of conventional methods such as extraction process, prolonged color development, and use of concentrated acids. The boron concentration was measured spectrofluorimetrically with the prepared sensor. It is also a great advantage that the fluorescence sensor can be regenerated in a short time using distilled water. Moreover, the same sensor could be used 565 times for boron determination. The values of LOD and LOQ were $2.9x10^{-8}$ mol $L^{-1}$ and 9.66 $10^{-8}$ mol $L^{-1}$, respectively. Another advantage is that the sensor allows the determination of boron even in the presence of many foreign ions. It was found that the results were satisfactory when the boron concentration in the environmental water samples was analyzed by the developed sensor and ICP-OES method.

## REFERENCES

1. Garrett DE. Borates: handbook of deposits, processing, properties, and use. San Diego: Academic Press; 1998. 483 p.

2. Stellman JM, International Labour Organisation, editors. Encyclopaedia of occupational health and safety. 4th ed. Geneva: International Labour Office; 1998. 2 p.

3. Edition F. Guidelines for drinking-water quality. WHO chronicle. 2011;38:104–108.

4. Organization WH, others. Boron (Environmental health criteria monograph 204). World Health Organization, IPCS, Geneva, Switzerland. 1998;

5. Zaijun L, Zhu Z, Jan T, Hsu C-G, Jiaomai P. 4-Methoxy-azomethine-H as a reagent for the spectrophotometric determination of boron in plants and soils. Analytica Chimica Acta. 1999 Dec;402(1–2):253–7.

6. Aznarez J, Ferrer A, Rabadan J, Marco L. Extractive spectrophotometric and fluorimetric determination of boron with 2, 2, 4-trimethyl-1, 3-pentanediaol and carminic acid. Talanta. 1985;32(12):1156–1158.

7. Balogh IS, Andruch V, Kádár M, Billes F, Posta J, Szabová E. A simple method of boron determination in mineral waters using Victoria blue 4R. International Journal of Environmental Analytical Chemistry. 2009 May 15;89(6):449–59.

8. Rice EW, American Public Health Association, editors. Standard methods for the examination of water and wastewater. 22. ed. Washington, DC: American Public Health Association; 2012. 1120 p.

9. Marcantonatos M, Gamba G, Monnier D. Contribution à l'étude du dosage de traces d'acide borique par luminescence. Helvetica Chimica Acta. 1969;52(2):538–43.

10. Campaña AMG, Barrero FA, Ceba MR. Spectrofluorimetric determination of boron in soils, plants and natural waters with Alizarin Red S. The Analyst. 1992;117(7):1189–91.

11. SARICA DY, ERTAŞ N. Flow injection analysis for boron determination by using methyl borate generation and flame atomic emission spectrometry. Turkish Journal of Chemistry. 2001;25(3):305–310.

12. Çetinkaya E, Dönmez KB, Deveci S, Doğu M, Şahin Y. Determination of plant available boron in agricultural soil by using voltammetric method. EURASIAN JOURNAL OF SOIL SCIENCE (EJSS). 2014 Sep 1;3(3):182.

13. Liv L, NAKİBOĞLU N. Simple and rapid voltammetric determination of boron in water and steel samples using a pencil graphite electrode. Turkish Journal of Chemistry. 2016;40(3):412–421.

14. Ohyama S, Abe K, Ohsumi H, Kobayashi H, Miyazaki N, Miyadera K, et al. Fully Automated Measuring Equipment for Aqueous Boron and Its Application to Online Monitoring of Industrial Process Effluents. Environmental Science & Technology. 2009 Jun;43(11):4119–23.

15. Hill CJ, Lash RP. Ion chromatographic determination of boron as tetrafluoroborate. Analytical Chemistry. 1980 Oct;52(1):24–7.

16. Brennan MC, Svehla G. Flow injection determination of boron, copper, molybdenum, tungsten and zinc in organic matrices with direct current plasma optical emission spectrometry. Fresenius' Zeitschrift für Analytische Chemie. 1989;335(8):893–9.

**Commented [SC1]:** für içindeki ü harfi yerine "?" vardı