Rapid and Accurate Validated Potentiometric Method for Bispyribac Herbicide Assessment in Rice and Agricultural Wastewater

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Abstract: A new validated method based on potentiometric transduction for bispyribac herbicide assessment in commercial formulations, rice and wastewater samples is fabricated and characterized. Sensors are based in terms of their fabrication on tridodecyl methyl ammonium chloride (TDMAC) as recognition material. TDMAC was plasticized in a poly (vinyl chloride) (PVC) matrix to prepare the membrane. Under static modes of operation, the sensors revealed a Nernstian anionic slope of 

\[-63.6 \pm 0.7 \text{ mV/decade}\]

within a linear range of 9.1 \times 10^{-6} – 1.0 \times 10^{-2} in 50 mM phosphate buffer solution (PBS), pH7. The detection limit was 6.0 \times 10^{-6} M. The sensor was successfully introduced in a flow-stream system revealing a Nernstian response of 

\[-53.8 \pm 1.3 \text{ mV/decade}\]

over a linear range of 2 \times 10^{-4} – 1.0 \times 10^{-2} M and lower detection limit of 5.6 \times 10^{-5} M. The sampling rate was calculated to be (~42 sample/h). Validation of the assay method is presented in detail including accuracy, trueness, bias, between-day variability and within-day variability, and good performance characteristics of the method are obtained. The presented method was successfully introduced to bispyribac determination in different complex matrices such as commercial bispyribac sodium known as (Nominee-kz, 3% soluble liquid (SL)), rice samples and agricultural wastewater samples. The samples were analyzed successfully under both static and hydrodynamic modes of operation. The results obtained were in a good agreement with those obtained by the liquid chromatographic method.

Keywords: potentiometric sensors; PVC membrane sensors; bispyribac; flow-injection analysis (FIA); method validation

1. Introduction

Herbicides are considered as a type of pesticide that can be used for controlling undesired weeds growth [1]. Bispyribac-sodium (or else sodium 2,6-bis [(4,6-dimethoxy-2-pyrimidinyl) oxy] benzoate) (Figure 1) is the most common recommended herbicides for rice weed and a pyrimidinyl carboxy herbicide with broad spectrum and large effect. It has been registered in Egypt for use in irrigated rice cultivation and it is also recommended in rice cultivation in other countries such as the United States.
and Brazil [2]. The herbicide inhibits the efficiency of the enzyme acetolactate synthetase, which affects plant growth. Therefore, bispyribac has been used for post-emergence control of a broad range of weeds [3–5]. Although bispyribac is of low-toxicity, its overuse has negative effects on human health, wildlife, and the environment [6]. It has acidic characteristics (i.e., pKa = 3.05), is highly soluble in water (73,300 mg/L) and its half-life in soil is <10 days [2,7]. In addition, it presents a lethal dose of 3524 mg/kg when introduced orally in rats, and presents CL50 for trout (96 h) > 100 mg/L and CL50 for Daphnia (48 h) > 100 mg/L [8,9].

There are several analytical methods reported in literature for bispyribac determination. These methods include liquid chromatography [10–12], liquid chromatography coupled to mass spectrometry [13,14], and high-performance liquid chromatography in conjunction with diode array detection (HPLC-DAD) [2,15]. Although many of these methods offered high sensitivity and selectivity, but they possess a lot of limitations. They were time-consuming, complicated in operation, required high-cost instrumental set up and mainly required sample pre-treatments. Therefore, it is necessary to find a rapid, simple, easy, sensitive, selective and cost-effective method for detecting this herbicide. Electrochemical sensors have become an attractive cost-effective tool for reliable and fast trace-level environmental assessment. Among of these sensors, ion-selective electrodes (ISEs) based on potentiometric transduction offered core features like excellent selectivity, ease of use, high reliability and no sample pre-treatment is required [16–19]. It has been noticed that most of these potentiometric electrodes have been used to monitor inorganic ions [20–25], but electrodes based on potentiometric transduction have not been reported widely to measure organic anions [26–30]. For bispyribac determination, only one potentiometric sensor is reported in the literature by our group [31].

Lipophilic quaternary ammonium salts (QAS) are successfully and extensively used as extracting agents and as sensory recognition materials in potentiometric selective electrodes [32,33]. The potentiometric selectivity is influenced by the structural features of the quaternary ammonium cation, in particular, steric accessibility of its exchange center [34].

In the present work, new liquid-contact sensors based on potentiometric transduction are designed and characterized for bispyripac monitoring. The membrane based sensors are fabricated upon using tridodecyl methyl ammonium chloride (TDMAC) as a recognition sensory element after its dissolution in plasticized poly (vinyl chloride) (PVC) membrane with o-NPOE as a solvent mediator. The sensors are examined, characterized and used to determine bispyribac in the commercial formulation, rice and wastewater samples under static and hydrodynamic modes of operation (FIA). Validation of the presented method is shown in details including accuracy, trueness, bias, between-day variability and within-day variability, and good performance characteristics of the method are obtained.
2. Material and Methods

2.1. Apparatus

All potentiometric bispyribac measurements were carried with using bench pH/mV meter (Jenway™ 3510, London, UK). The potentiometric cell was constructed using the presented bispyribac sensor and Jenway™ Ag/AgCl double junction reference electrode which filled with 0.1 M CH₃COOLi solution in its outer compartment. All pH measurements were totally performed using a glass pH electrode (Orion 81-02, MA, USA). The response signals were measured in stirred different bispyribac solutions. The electrochemical cell is presented as: Ag/AgCl/10⁻³ M (bispyribac)/bispyribac-sensing membrane/bispyribac test solution/double junction Ag/AgCl reference electrode.

For the flow system, a two-channel peristaltic pump (Ismatech MS-REGLO) was used, in conjunction with Omnifit injection valve (Rheodyne, MA, USA, Model 7125) and loop volume sample of 100 µL. Polyethylene tubing (Tygon, 0.7 mm i.d.) was used for solution transfer under 3 mL/min flow rate. The response signals were processed using pH/mV meter (Orion SA 720, MA, USA) connected to data processor through an external interface (Pico Technology, London, UK, model ADC 16) and Pico Log operating software for Windows (Pico Technology, UK, version 5.07).

2.2. Reagents and Chemicals

All chemicals and reagents used were of analytical grade and high purity. High molecular weight PVC, o-nitrophenyloctyl ether (o-NPOE), tetrahydrofuron (THF) and tetradodecylmethyl ammonium chloride (TDMAC) were supplied by Sigma-Aldrich St. Lois, USA. All pesticides and herbicides such as bispyribac Sodium (99%), Methomyl (98.5%), oxamyl (99%), diquate dibromide (98.3%), dimethoate (98%) and cyromazine (98.5%) were purchased from Ehrenstorfer GmbH (Berlin, Germany). Commercial bispyribac sodium known as Nominee-kz, 3% soluble liquid (SL) was obtained from Kafr El-Zayat pesticides and chemicals company (Gharbia, Egypt).

All bispyribac solutions were prepared in 50 mM phosphate buffer solution (PBS) and the ionic strength of all solutions was adjusted using 0.1 M NaCl.

2.3. Sensor Construction and Potential Measurements

Bispyribac membrane based sensor was prepared as previously mentioned [35,36]. A 3 mg of TDMAC ion-exchanger as a sensory element, 132 mg of o-NPOE as a plasticizer and 66 mg PVC, and all are dissolved in ~3 mL THF. The mixture solution was introduced into a 2.2 cm Petri-dish and is allowed to stand overnight for complete solvent evaporation. Discs of 3-mm diameter were cut from the (master membrane) and glued by THF to the flat end of the plastic PVC tubing. A 10⁻³ M of bispyribac solution was used as an internal filling solution followed by the insertion of a 3-mm-diameter Ag/AgCl-coated wire as an internal reference electrode. Conditioning of the prepared sensor was carried out after soaking the sensor in 10⁻³ M bispyribac solution for 24 h before use. It was stored in the same solution when not in use. Calibration of the presented sensor was carried out after immersion of the potentiometric cell into a 25-mL beaker containing 9.0 mL of 50 mM PBS. An aliquot (i.e., 1.0 mL) of 10⁻²–10⁻⁶ M standard bispyribac solutions was successively added and the solution stirred. The potential response was measured, recorded and plotted against the logarithm of bispyribac concentrations.

For continuous monitoring using the flow injection system, the sensing membrane was prepared containing the same membrane compositions as mentioned above. The membrane cocktail was drop-casted using a micro-dropper into a small hole (3 mm wide) made in the middle of a Tygon tube with a 5-cm length. After complete dryness of the formed membrane, the tube was then inserted into a blue pipette-tip and the detector was inserted into the flow-injection system (Figure 2). A carrier stream of 50 mM PBS solution, pH 7.0, was then pumped at a constant flow rate of 3.0 mL/min. The sensor was located in conjunction with an Ag/AgCl double junction-reference electrode. A real-earth link was connected to the reference electrode connection to prevent minor pulsation resulting from the
peristaltic pump. After a stable baseline was achieved, the potential was recorded versus time to construct the calibration plot.

**Figure 2.** Flow-injection setup: (1) 30 mM phosphate buffer solution (PBS) reservoir (pH 7), (2) peristaltic pump, (3) injection valve, (4) cell assembly, (5) waste reservoir (6) flow-through half cell containing bispyribac-poly (vinyl chloride) (PVC) membrane and Ag/AgCl internal reference electrode.

**2.4. Bispyribac Determination in Commercial Formulation Samples**

The presented sensor was applied for the determination of bispyribac content in commercial pesticide formulation (i.e., Nominee-kz, 3% soluble liquid (SL)) purchased from the local market. Appropriate volumes of the formulation sample were introduced to a 100-mL measuring flask and then diluted to the mark with 50 mM PBS of pH 7. For batch assessment, 10-mL aliquots of the diluted formulation solutions were potentiometrically measured using the proposed sensor. The potential readings of each unknown bispyribac samples were recorded and the concentration was then calculated using the constructed calibration plot.

For continuous bispyribac measurement, a flow stream of 50 mM PBS solution, pH 7.0 as a carrier solution was pumped to pass through the flow-cell at a flow rate 3 mL/min, the bispyribac test solutions were then injected in triplicates into 100 µL injection sample loop, and the average potential readings were then compared with the constructed calibration plot.

**2.5. Determination of Bispyribac in Spiked Rice Samples**

Constant weights (i.e., 2.0 g) of well-ground blank rice samples were spiked with 10 mL aliquots of bispyribac sodium solutions in the concentration range (10–20 µg/mL). The homogenates were mixed in 15 mL polypropylene sample tubes and sonicated for 5 min. The spiked samples were centrifuged at 3500 rpm for 20 min and then the supernatant liquid was transferred into a 25-mL beaker. The sample solutions were subjected to determine bispyribac content under both static and hydrodynamic mode of operations. The values of the potential for these spiked samples were recorded, and the concentration of bispyribac was calculated from the corresponding regression equations and then the percentage of the recoveries was calculated.

**2.6. Bispyribac Determination in Agricultural Wastewater**

The developed method was applied to determine bispyribac in agricultural wastewater samples. The wastewater samples were collected up to 30 days after the application of bispyribac herbicide at the recommended dose (50 g bispyribac-sodium/ha).
3. Results and Discussion

3.1. Performance Characteristics of Sensors

Liquid-contact bispyribac polymeric membrane sensors based on the anion exchanger tridodecyl methyl ammonium chloride (TDMAC) plasticized in o-NPOE were presented. The sensors were prepared and characterized according to the International Union of Pure Applied Chemistry (IUPAC) [37]. As shown in Figure 3, the sensors offered a good Nernstian response toward bispyribac anion within the linear concentration range of $9.1 \times 10^{-6} - 1.0 \times 10^{-2}$, detection limit of $6.0 \times 10^{-6}$ M, and potentiometric slope of $-63.6 \pm 0.7$ ($r^2 = 0.9971$) mV/decade. For the proposed sensors, all potentiometric performances were presented in Table 1. All subsequent experiments were made with this sensor.

![Figure 3](image.png)

**Figure 3.** Time-dependent potential response trace; inset [calibration curve of the tridodecyl methyl ammonium chloride (TDMAC)-based bispyribac-ion-selective electrode (ISE) under static conditions.

**Table 1.** Performance characteristics of bispyribac PVC membrane sensor in 50 mM PBS (pH 7) under static and hydrodynamic modes of operation.

| Parameter                              | Batch           | Flow-Through Analysis |
|----------------------------------------|-----------------|-----------------------|
| Slope, mV/decade                       | $-63.6 \pm 0.7$ | $-53.8 \pm 1.3$       |
| Correlation coefficient, ($r^2$)       | 0.9971          | 0.9983                |
| Linear range, M                        | $9.1 \times 10^{-6} - 1.0 \times 10^{-2}$ | $2 \times 10^{-4} - 1.0 \times 10^{-2}$ |
| Detection limit, M                     | $6.0 \times 10^{-6}$ | $5.6 \times 10^{-5}$ |
| Response time for $10^{-5}$ M, s       | 5               | 10                    |
| Recovery time for $10^{-5}$ M, s       | 10              | 50                    |
| Working acidity range, pH              | 6–8             | 6–8                   |
| Accuracy, %                            | 99.3            | 98.6                  |
| Trueness, %                            | 99.1            | 98.2                  |
| Bias, %                                | 0.9             | 1.3                   |
| Within-day Repeatability, CV$_w$, %   | 0.6             | 1.1                   |
| Between days-variation, CV$_b$, %      | 1.1             | 1.3                   |
| Relative Standard deviation, %         | 0.7             | 0.9                   |
| Precision, %                           | 1.1             | 1.5                   |

The pH effect on the response behavior of the bispyribac sensor was checked by varying the pH of $1.0 \times 10^{-3}$ M and $1.0 \times 10^{-4}$ M bispyribac solution from pH 2 to 11 using concentrated NaOH and/or H$_3$PO$_4$ solutions. After each addition, the corresponding potential readings at each pH value
were recorded. As shown in Figure 4, the sensor’s response was kept constant over the pH range 6 to 8. Below this range, the sensor potential was sharply increased due to the formation of un-ionized bispyribac or interference coming from H⁺ ion concentration. At high pH values > 8, the sensor responded to OH⁻-ion. A 50 mM phosphate buffer solution of pH 7, containing 10⁻² M NaCl was used as a background solution and used for all subsequent measurements.

![Figure 4. pH effect on the potentiometric behavior of bispyribac membrane-based sensor.](image)

The unbiased potentiometric selectivity coefficients (\(K_{Pot}^{bispyribac, J}\)) of the bispyribac sensor were evaluated according to the method presented by Bakker (Modified separate solution method, MSSM) [38]. All potentiometric selectivity coefficients of the proposed sensor over different herbicides are summarized in Table 2. Typical selectivity order for the proposed sensor was: The typical selectivity order of ISE sensor (I) is: BIS⁻ > sulphadimidine > 3-aminophenol > cyrmazine > phenol > SCN⁻ > I⁻ > SO₄²⁻ > SO₃²⁻ > dimethoate > methomyl > oxamyl > CH₃COO⁻ > diquate dibromide.

| Interfering Ion, J | \(\log K_{Pot}^{bispyribac, J}\) of the Proposed Sensor |
|-------------------|-----------------------------------------------------|
| SCN⁻              | -2.50                                               |
| SO₄²⁻             | -5.10                                               |
| SO₃²⁻             | -4.29                                               |
| I⁻                | -3.17                                               |
| CH₃COO⁻           | -5.72                                               |
| Phenol            | -2.13                                               |
| 3-aminophenol     | -1.21                                               |
| Sulphadimidine    | -1.13                                               |
| Cyromazine        | -1.24                                               |
| Diquate dibromide | -5.77                                               |
| Methomyl          | -4.78                                               |
| Dimethoate        | -4.47                                               |
| Oxamyl            | -5.39                                               |

3.2. Flow Injection Analysis (FIA) Measurements

Flow injection analysis (FIA) of different bispyribac calibration solutions using a tubular-type detector incorporating a TDMAC was made. The calibration data revealed a wide linear range over the range 2 × 10⁻⁴–1.0 × 10⁻² M with a detection limit 5.6 × 10⁻⁵ M and a potentiometric slope of −53.8 ± 1.3 mV/decade. Low detection of bispyribac concentration and the wide linear range of measurements allowed accurate determination of bispyribac in a variety of real samples.
Typical transient flow injection signals for different bispyribac concentrations are shown in Figure 5. The sampling rate analysis was found to be 40–44 runs/h. This automatic technique offered a simple and fast viable tool for bispyribac determination in view of the absence of any commercial bispyribac sensor.

![Figure 5. Transient potentiometric flow injection signals for bispyribac standards using the proposed sensor.](image)

**3.3. Response Time and Stability**

The time required to attain 95% of the equilibrium potential value at fixed concentration is known as the dynamic response time of a sensor. This value indicates the online-detection suitability of the presented sensor and the ease of its introduction in an automated system. Time response was calculated after potential readings recording at 10 s time intervals after a 10-fold increase in bispyribac concentration. As shown in Figure 3, the sensor reached the potential equilibrium within less than 5 s following the concentration changes, revealing a rapid and fast response.

To test the life span and stability of the presented electrode, it was exposed to air for 3 months at ambient temperature. The calculated relative standard deviation (RSD) of the observed potential response was <5%. This can demonstrate the suitable stability of the sensor and its successful application for practical analysis.

**3.4. Validation of the Presented Method**

**3.4.1. Calibration Curve, Linearity and Detection Limit**

Over six concentration levels (triplicate measurements for each concentration), the equation of linear regression was: \( y (\text{mV}) = -63.6x + 336 \), where \( y \) = potential (mV), \( x \) = bispyribac concentration (M), with a correlation coefficient \( r^2 = 0.997 \). From the calibration plot, the linearity of the proposed method was calculated, revealing a linear interval in the range of \( 9.1 \times 10^{-6} \) to \( 1.0 \times 10^{-2} \) M and \( 2 \times 10^{-4} \) to \( 1.0 \times 10^{-2} \) M with near-Nernstian slopes of \(-63.6 \pm 0.7 \) mV/decade and \(-53.8 \pm 1.3 \) mV/decade for the static and hydrodynamic mode of operations, respectively. The lower limit of detection (LOD) of the presented method was found to be \( 6.0 \times 10^{-6} \) M and \( 5.6 \times 10^{-5} \) M for the static and hydrodynamic modes of operation, respectively.

**3.4.2. Precision (Repeatability and Intermediate Precision) and Accuracy (Recovery)**

Different internal quality control bispyribac samples containing (5, 10, 100, 200 and 300 \( \mu \)g/mL bispyribac, \( n = 6 \), each) were used for relative standard deviation (RSD) calculations. Repeated
measurements showed RSD values in the range of 1.1 ± 0.7–1.5 ± 0.4% for static and hydrodynamic mode of operations, respectively.

Precision (%) was calculated according to equation Equation (1).

\[ \text{Precision, \%} = \left( \frac{S}{X} \right) \times 100 \]  

where: \( X \) is the mean of test results obtained for the bispyribac reference standard sample and \( S \) is the standard deviation of \( X \).

The degree of the closeness of test results obtained by the presented electrode with the true value of bispyribac solution was measured by adding (spiking) of a known amount of bispyribac (reference samples). The accuracy of the assay method was calculated using Equation (2) and found to be 99.3 ± 0.7–98.6 ± 1.1% for static and hydrodynamic mode of operations, respectively.

\[ \text{Accuracy, \%} = \left[ \frac{(X_s - X)}{X_{\text{add}}} \right] \times 100 \]  

where: \( X_s \) is the mean result of the added (spiked) bispyribac solution, \( X \) is the mean result of the test sample (un-spiked bispyribac samples) and \( X_{\text{add}} \) is the amount of added bispyribac standard.

3.4.3. Trueness and Bias

Under replicate analyses, different bispyribac reference samples (5, 10, 100, 200 and 300 \( \mu \)g/mL bispyribac) were used to check the method trueness and bias according to Equations (3) and (4), respectively.

\[ \text{Trueness, \%} = \left( \frac{X}{\mu} \right) \times 100 \]  
\[ \text{Bias, \%} = \left[ \frac{(X - \mu)}{\mu} \right] \times 100 \]  

where: \( X \) is the mean of results obtained for the reference bispyribac sample and \( \mu \) is the true value of this sample. The mean trueness and bias percentages obtained, ranged between 99.1 ± 0.8–98.2 ± 1.4% and 0.9 ± 0.02–1.3 ± 0.8% for static and hydrodynamic mode of operations, respectively.

3.4.4. Data Repeatability and Reproducibility

The results distribution (data spread) was obtained when a bispyribac sample (10–300.0 \( \mu \)g/mL bispyribac) was measured in the same day (repeatability) and on different days (reproducibility) to conform the data closeness between those obtained with the bispyribac reference sample under different conditions with different sensor assembly and different instruments at different times. The reproducibility \( (R) \) is calculated from the standard deviation data of the results \( (S_R) \) (Equation (5)).

\[ R = 2.8 \times S_R \]  

where 2.8 = 2\( \sqrt{2} \), and is derived from the normal or Gaussian distribution; ISO 5725). The data of reproducibility within-day and between-days were found to be 0.6 ± 0.03–1.1 ± 0.4% and 1.1 ± 0.2–1.3 ± 0.5%, respectively.

3.5. Determination of Bispyribac Sodium (BIS\textsuperscript{−}) in Commercial Formulation Sample

The presented method was successfully applied for the determination of bispyribac content in Nominee-kz, 3% soluble liquid (SL) formulation under both batch and flow-through analysis. The results were compared to the method of high-performance liquid chromatography (HPLC) (Table 3) [12].
Table 3. Determination of bispyribac in commercial herbicide formulation.

| Commercial Product | Label (w/v%) | * Found Potentiometry, (Bispyribac Sensor) | HPLC Method [12] |
|--------------------|--------------|------------------------------------------|-------------------|
|                     |              | Batch | Flow Analysis |                     |
| Nomenee-kz, Kafr El-Zayat Pesticides and Chemicals Company (Gharbia, Egypt) | 3 | 2.83 ± 0.6 | 2.74 ± 0.8 | 2.93 ± 0.3 |

* Average of 5 measurements.

3.6. Determination of Bispyribac in Different Spiked Rice Samples

Application of the method for bispyribac assessment in rice samples were checked by spiking aliquots of different rice samples with a known concentration of standard bispyribac solution. A 10-mL of bispyribac concentration (10–20 µg/mL) was spiked into 2.0 gm of rice samples to evaluate the method procedure and recovery (%) using Equation (2). The average recoveries for the proposed sensor were 97.1% and 97.6% under both batch and flow injection analysis, respectively. All obtained results were shown in Table 4 and showed good recoveries in the determination of bispyribac under both static and hydrodynamic modes of operation in different rice samples. This confirms that the presented method is being simple, rapid, and good tool for the determination of bispyribac in different matrices.

Table 4. Batch and flow injection determination of bispyribac in different spiked rice samples.

| Sample | Amount Added, µg/mL | * Amount Found, µg/mL |
|--------|----------------------|------------------------|
|        |                     | Static Mode            | Hydrodynamic Mode | HPLC [33] |
|        |                      | Found                  | Recovery,%        | Found | Recovery,% | Found | Recovery,% |
| Sample 1 | 10  | 9.3 ± 0.5 | 93 | 9.5 ± 0.3 | 95 | 9.7 ± 0.2 | 97 |
| Sample 2 | 15  | 13.7 ± 1.1 | 91.3 | 14.1 ± 0.9 | 94 | 14.6 ± 0.3 | 97.3 |
| Sample 3 | 20  | 21.4 ± 1.5 | 107 | 20.8 ± 1.2 | 104 | 20.2 ± 0.1 | 101 |

* Average of 5 measurements.

3.7. Bispyribac Determination in Agricultural Wastewater Samples

To test the applicability of the presented method, the sensors were used for bispyribac determination in different agricultural wastewater samples. The samples were collected over 30 days after the application of bispyribac herbicide to agricultural lands planted with rice and sprayed with this herbicide at the recommended dose (50 g bispyribac-sodium/ha). The samples were introduced to the proposed methods and measured under both static and hydrodynamic modes of operation. The samples were also measured by the HPLC method for comparison. The results obtained were in a good agreement between those obtained by the recommended potentiometric method and those obtained using the HPLC method (Table 5). It can be noticed that the presented potentiometric methods have promising feasibility for the bispyribac quantification in different complex samples.

Table 5. Assessment of bispyribac in different wastewater samples.

| Sample | * Amount Found, µg/mL |
|--------|------------------------|
|        | Static Mode | Hydrodynamic Mode | HPLC [33] |
| Sample 1 | 3.2 ± 0.2 | 2.8 ± 0.6 | 2.9 ± 0.1 |
| Sample 2 | 3.7 ± 0.1 | 4.1 ± 0.2 | 3.5 ± 0.1 |
| Sample 3 | 1.1 ± 0.5 | 1.4 ± 0.3 | 1.2 ± 0.4 |
| Sample 4 | 2.5 ± 0.7 | 2.9 ± 0.6 | 2.2 ± 0.1 |

* Average of 5 measurements.
4. Conclusions

A novel validated method was employed based on potentiometric transduction for bispyribac determination in commercial formulation, rice and wastewater samples. The method is based on the prepared and characterized of polymeric PVC membrane sensor. The sensor was constructed using tridodecyl methyl ammonium chloride (TDMAC) as anion exchanger and as an electroactive material. In both conventional batch and flow injection analysis, the method covered the range $9.1 \times 10^{-6} - 1.0 \times 10^{-2}$ M with a low detection limit of $6.0 \times 10^{-6}$ M. Fast, stable and selective response of the sensors toward bispyribac anion was obtained. No interferences were caused by most ions and herbicides that commonly present in the environment. The originality of the presented sensor is presented in its introduction in an automated flow-through system, and it is simple, inexpensive, precise, accurate and easy to apply. The method has only one limitation in which it presents higher detection limit than previously reported by our group [31]. The tubular devices are particularly suitable for routine applications and facilitate the determination of bispyribac with high sampling rates, and a low consumption of sample volume.

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