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Development and Validation of Spectrophotometric Method for Determination of Oxyfluorfen Herbicide Residues

Khansaa Fatta Alrahman[1], Abdala A Elbashir[1]* and Hassan El-obid Ahmed[1,2]

[1]*Chemistry Department, Faculty of Science, University of Khartoum, Khartoum, Sudan*
[2]*Chemistry Department, Faculty of Science, Gassim University, Kingdom of Saudi Arabia*

Abstract

Simple spectrophotometric method has been developed and validated for the determination of oxyfluorfen herbicide residues. The proposed method is based on the formation of an orange charge- transfer complex between oxyfluorfen pesticide as electron donor and 1,2- naphthoquinone-4-sulphonate (NQS) as electron acceptor. In basic medium pH 13.0, an orange colored product exhibiting maximum absorption peak (λ_{max}) at 460 nm. The variables that affected the reaction such as pH, concentration and volume of NQS reagent, amount of buffer solution and reaction time were carefully studied and optimized. Under the optimum conditions, Beer's law is obeyed in the range 0.4-4.0 µg/mL of oxyfluorfen. The linear regression equation of the calibration curve is A=0.0906+0.2579 c (µg/mL), with a linear regression correlation coefficient of 0.9993. The molar absorptivity was 1.33 × 10^5 l/mol cm. The limits of detection (LOD) limits of quantification (LOQ) were found to be 0.12 µg/ mL, 0.36 µg/mL, respectively. The recovery rate is in the range of 93.50-103.00% was obtained. The proposed method has been successfully applied to the determination of oxyflourfen pesticide residues in tomato, onion and water with good accuracy and precision.

Keywords: Oxyfluorfen; 1,2-naphthoquinone-4-sulphonate (NQS); Charge-transfer; spectrophotometry; Pesticide residues analysis

Introduction

Oxyfluorfen is a diphenyl ether herbicide (Figure 1a), acting as a protoporphyrinogen oxidase inhibitor and used for pre- or post-emergence to control monocotyledonous and broad- leaved weeds at rate in the range 0.25-2.0 kg of active ingredient (a.i.) per hectare. The herbicide is degraded at temperature >50°C [1]. As oxyfluorfen is not metabolized in plants and is subjected to very little translocation, phototransformation is suggested as a possible abiotic degradation process. Solubility in water is 0.1 mg l^{-1}. Half-life in soil approximately ranges 30-56 days. The organic matter content of soil seems to influence oxyfluorfen persistence and activity [2-6].

European Community Directive fixes allowable levels of pesticides in drinking water to 0.1 ng/mL for individual pesticide and some of their degradation products, and 0.50 ng/mL for the sum of all pesticides [7]. Therefore, it is of essential importance to set up reliable and efficient methods to determine the residues of pesticides in various water environments at trace levels.

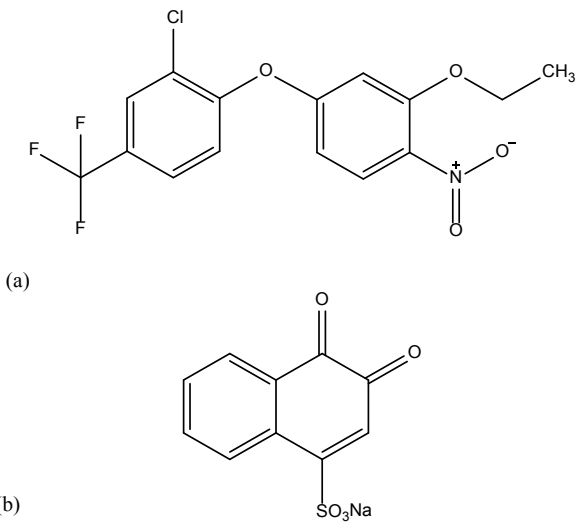

Figure 1: Chemical structure of (a) Oxyflourfen (b) 1, 2-naphthoquinone-4-sulfonate (NQS).

Different chromatographic methods have been reported for the analysis of oxyfluorfen in food and environmental samples. These methods includes analysis of oxyfluorfen in water and soil with gas chromatography-electron capture detector (GC-ECD) [8], and gas liquid chromatography with tandem mass spectrometry (GC-MS/MS) for analysis of oxyfluorfen in olive oil [9]. GC-MS and GC-ECD method for routine analysis of oxyfluorfen in thyme [10], high performance liquid chromatography (HPLC) [11,12]. However these sophisticated instrumental techniques are very expensive and requiring special training not available in developing countries.

1,2-naphthoquinone-4-sulfonate (NQS) (Figure 1b) has been used as a color-developing reagent in the spectrophotometric determination of many pharmaceutical amines [13-26]. In depth review regarding the applications of NQS for determination of pharmaceutical bearing amine group has recently been reviewed by Elbashir et al. [21].

A few methods have been reported for the use of NQS as chromogenic reagent in spectrophotometric determination of pesticides residues [27].

Washing and boiling are considered to be as efficient methods for removing pesticides residues from different vegetables. Several studies have examined the effects of washing on removing pesticide residues were reported [28-31].

However, such studies on the uses of naphthoquinone derivatives, as acceptors are quite sparse such as spectroscopic study of interaction

***Corresponding author:** Abdala A. Elbashir, Chemistry Department, Faculty of Science, University of Khartoum, Khartoum, P.O. Box 321, 1115, Sudan, E-mail: aaelbashir@uofk.edu

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between 2,3-dichloro-1,4-naphthoquinone (DClNQ) as electron acceptor and n-butylamine as electron donor [32]. The reaction between NQS and oxyfluorfen has not investigated yet. Therefore, this study was devoted to investigate the reaction between NQS and oxyfluorfen, and use this colored reaction in development of simple rapid spectrophotometric method for determination of oxyfluorfen residues in tomato fruit, onion and water samples. Moreover the effect of washing and boiling on the removal of the oxyfluorfen from tomato fruit, onion was also investigated by the developed method.

Experimental

Instrumentation

All the spectral measurements were carried out by using a Double beam UV 1800 ultraviolet-visible spectrophotometer model Shimadzu 1800, with quartz cells of 1 cm optical path length. pH meter model pH 211(HANNA Italy) was used for pH measurements.

Chemicals

All chemicals used were of analytical-reagent grade. Distilled water was used to prepare all solutions.

Stock standard solution of oxyfluorfen (100 µg/mL): An accurately 0.01 g of oxyfluorfen standard was dissolved in absolute ethanol, transferred into a 100 mL volumetric flask and diluted to the mark with absolute ethanol and mixed well. This stock solution was further diluted with distilled water to obtain working solutions in the ranges of 0.4-4.0 µg/mL.

1,2-naphthoquinone-4-sulfonate (NQS) was obtained from (Aldrich Chemical Co., St., USA). A solution of (NQS) 0.5% (w/v) was prepared by dissolving 0.5 g in distilled water, transferred into a 100 mL volumetric flask and diluted to the mark with distilled water and mixed well. The solution was freshly prepared and protected from light during use.

Buffer solution of pH 13.0 was prepared by mixing 50 mL of 0.2 M aqueous solution of potassium chloride with 100 mL of 0.2 M aqueous solution of sodium hydroxide in 100 mL volumetric flask, and adjusted by pH meter.

Procedure of calibration

Accurately measured aliquots of oxyfluorfen solution containing 0.4-4.0 µg/mL were transferred into separate 10 mL volumetric flasks. 2.0 mL of NQS solution (0.5%) was added and followed by 1.5 mL buffer solution pH 13 (KCl-NaOH).

The reaction mixture was mixed well, completed to volume with distilled water. This solution was stood for 20 min at room temperature, the absorbance was measured at 460 nm against reagent blank treated similarly without oxyfluorfen.

Procedure for the determination of the Stoichiometric ratio of the reaction

Under the optimum conditions, the stoichiometry of the reaction between oxyfluorfen and NQS was investigated by Job's method of continuous variation [33]. Master equimolar (1.5×10^{-2} M) aqueous solution of oxyfluorfen and NQS were prepared. Series of 10 mL portions of the master solutions of oxyfluorfen and NQS were made up comprising different complementary proportions (0:10, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4,7:3, 8:2, 9:1, 10:0) in 10 ml volumetric flask containing 1.5 mL of buffer solution (pH 13), the solutions was further treated as described under the general recommended procedures.

Determination of oxyfluorfen in water samples

10 mL of distilled water were spiked with known amount of oxyfluorfen and kept for 30 min. Samples were extracted twice with chloroform (10 mL) in a separatory funnel. 15 g of anhydrous sodium sulphate was added to chloroform layer to eliminate residues of water. Then, extract was evaporated off under suction to dryness. Residue thus obtained was analyzed using the proposed method. Amount of oxyfluorfen was computed from the standard calibration curve.

Determination of oxyfluorfen in tomato and onion samples

Samples of tomato fruit or onion (50 g) free from pesticide were taken. Weighed samples were spiked with known amount of oxyfluorfen and kept for 4 hours. Samples were homogenized in blender with 40 mL chloroform for 3 min at 1800 rpm. The homogenized samples were filtered through 12 cm Buchner funnel with filter paper into 100 mL suction flask. The solid residues in blender jar were rinsed with two 10 mL portion of chloroform, and rinses were used to wash residues in Buchner funnel. The filtrate was transferred into 250 mL separatory funnel and two 20 mL portions of distilled water were added. 15 g of anhydrous sodium sulphate was added to chloroform layer to eliminate residues of water. Then, extract was evaporated off under suction to dryness. Residue thus obtained was analyzed using the proposed method. Amount of oxyfluorfen was computed from standard calibration curve.

Results and Discussion

Absorption spectrum of product

Oxyfluorfen is colorless solution, it's absorption spectrum was recorded against absolute ethanol. As can be seen in Figure 2, it was found that oxyfluorfen exhibits a maximum absorption wave length peak (λ_{max}) at 285 nm and the NQS was 360 nm. The reaction between oxyfluorfen and NQS was performed, and the absorption spectrum of the product was recorded against reagent blank. It was found that the product is an orange colored exhibiting (λ_{max}) at 460 nm. The (λ_{max}) of oxyfluorfen-NQS derivative was red shifted, eliminating any potential interference. Therefore, all measurements were carried out at 460 nm.

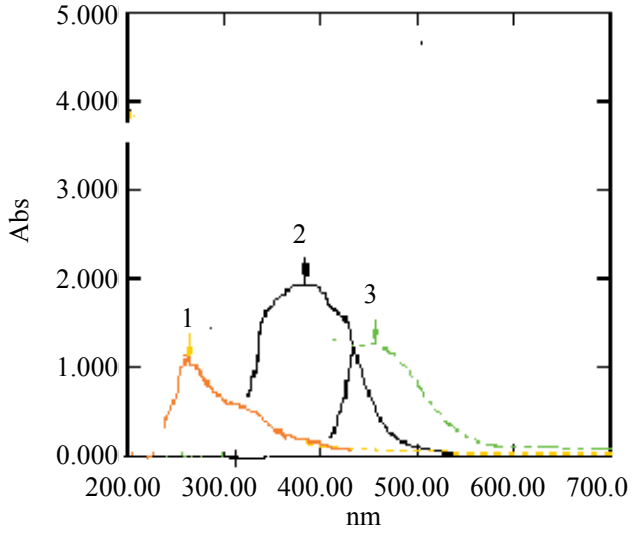


Figure 2: Absorption spectra of the system Oxyfluorfen-NQS (1) Absorption spectra of Oxyfluorfen (1.5 µg/mL) against absolute ethanol, (2) NQS against distilled water, (3) The reaction product of Oxyfluorfen (1.5 µg/mL) with NQS against reagent blank.

Optimization of reaction conditions

Effect of pH: The effect of pH on the system of oxyfluorfen-NQS was examined by varying pH from 6.0 to 14.0. As shown in Figure 3, the absorbance of the product is approximately stable in range of pH 6.0-11.0, which indicates that under these pH oxyfluorfen reacts very slowly with NQS. When pH is greater than 11.0, the absorbance begins to increase and becomes maximal at pH 13.0; this was occurred may to the ability of the formation of the final reaction product. At pH value more than 13.0, the absorbance of product was decreased.

Effect of amount of the buffer solution: The of amount of buffer solution on the absorbance of the product was investigated keeping pH at 13.0 the absorbance of product increases rapidly when the amount of the buffer is more than 1.0 mL, and becomes maximal when the amount of buffer solution is 1.5 mL. Then it becomes stable (data not shown). Therefore, 1.5 mL of buffer solution (pH 13) was selected as the optimum experimental condition.

Effect of NQS concentration: Keeping pH at 13.0, the effect of NQS concentration on the reaction was studied. The study revealed that the reaction was dependent on NQS concentration as seen in Figure 4. The absorbance of the reaction solution increased as the NQS concentration increased, the highest absorption intensity was attained at NQS concentration of 0.5% (w/v), and then the absorption value decreased. Therefore, the 0.5% (w/v) was selected to ensure the highest absorbance of the product.

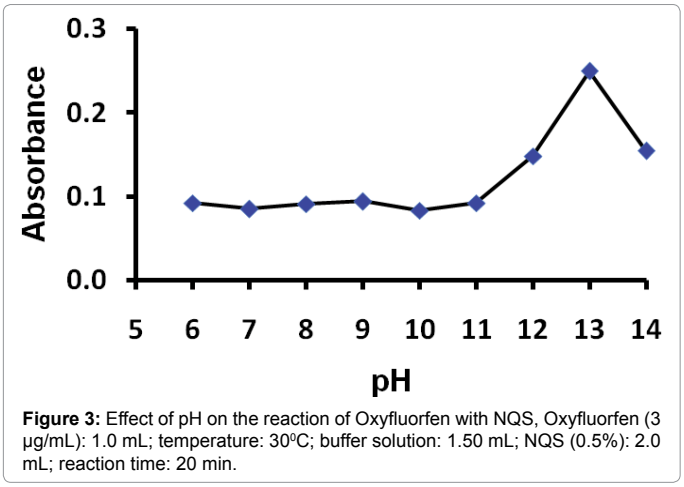


Figure 3: Effect of pH on the reaction of Oxyfluorfen with NQS, Oxyfluorfen (3 µg/mL): 1.0 mL; temperature: 30°C; buffer solution: 1.50 mL; NQS (0.5%): 2.0 mL; reaction time: 20 min.

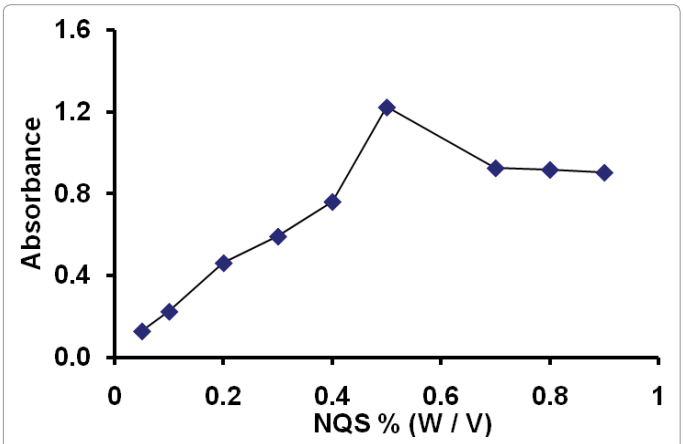


Figure 4: Effect of NQS concentration (w/v) on the reaction of Oxyfluorfen with NQS. Oxyfluorfen (3 µg/mL): 1.0 mL; temperature: 30°C; buffer solution (pH 13): 1.50 mL; NQS: 2.0 mL; reaction time: 20 min.

Effect of amount of the NQS reagent: The effect of the amount of NQS reagent (0.5% (w/v) on the absorbance of the product was also studied by varying the volume of NQS from 0.5-3.0 mL. The result shows that the absorbance of the product enhances rapidly with rise of amount of NQS solution, and becomes maximal when the amount of NQS solution is 2.0 mL. Then it becomes constant. Therefore, the amount of 2.0 mL NQS solution was selected to ensure the highest absorbance of product (data not shown).

Effect of standing time: According to the procedure, the effect of reaction standing time on the formation of the reaction product for oxyfluorfen was investigated by allowing the reaction to proceed for various time periods. The reaction carried out at 30°C. The result shows that the absorbance begins to increase and almost remains stable after 10 min.

The rapid increasing in absorbance after 10 min is indicative of formation of the final product, because the formation of the charge transfer product of n-π type is an instantaneous process, then it converts to the corresponding radical anion in the polar solvent. In addition, the absorbance of product remains stable for at least 1 hr. Therefore 10 min was selected as the optimum condition.

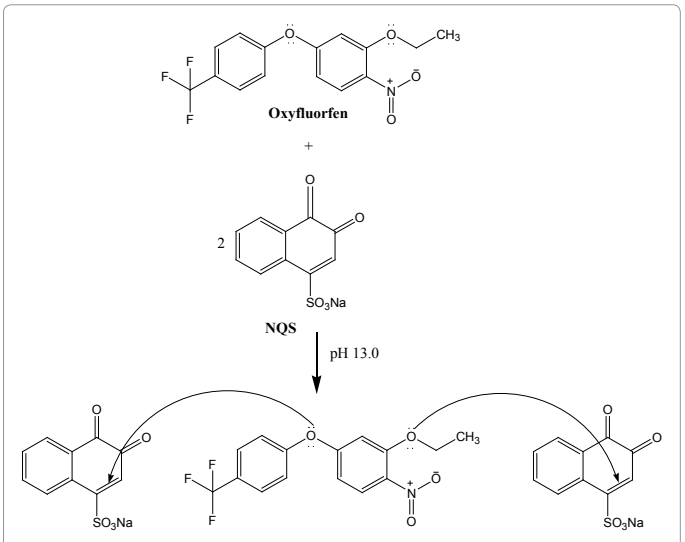
From all above experiments the optimum conditions were found to be pH 13.0, buffer volume 1.50 mL, NQS concentration 0.5%, NQS volume 2.0 mL, temperature 30°C and reaction time 10 min.

Discussion of reaction mechanism

According to literature reports, quinonyl [34] can act as electron acceptors with ethoxide/ methoxide ions [35] as electron donors that form charge transfer complex. Similarly oxyfluorfen (which contains two ether groups) reacts instantaneously with NQS as electron donor and electron acceptor at pH 13.0, to form an orange colored charge transfer product of n-π type, Scheme 1. This product is considered to be an intermediate molecular association complex which dissociate in the corresponding radical anion in the polar solvent.

The dissociation of the complex was promoted by the high ionizing power of the polar solvent (water). Owing to the stability and electron donating property of ether compounds is of significant use in such electron donor system. These ether compounds like 1,4-dimethoxybenzene are reported to undergo one electron transfer [35].

Furthermore, the molar ratio of oxyfluorfen to NQS in the reaction



Scheme 1: Proposed reaction pathway between Oxyfluorfen and NQS.

mixture was studied according to Job's method of continuous variation. The unsymmetrical bell shape of Job's plot confirmed that one molecule of oxyfluorfen reacts with two molecules of NQS, NQS: oxyfluorfen 2:1 (Figure 5). So it is concluded that oxyfluorfen which has two active centers (two ether groups capable for two electron donation) react with two NQS molecules (acceptors), respectively, to form an orange charge-transfer complex. Based on the observation molar ratio, the reaction pathway was postulated to proceed as shown in Scheme 1.

Validation of the method

Calibration curve, limit of detection (LOD) and limit of quantification (LOQ): Under the selected conditions, calibration curve for the determination of oxyfluorfen by it reaction with NQS was constructed by plotting the absorbance as a function of the corresponding concentrations. A linear relationship between the absorbance, A, of the product and the concentration, C, of oxyfluorfen is obtained in the range of 0.4-4.0 µg/ mL. The linear regression equation obtained from the calibration curve is:

A=0.0906+0.2579 C (µg /mL) with a correlation coefficient, r^2, of 0.9993 and a molar absorptivity of 1.33×10^5 L $mol^{-1}cm^{-1}$.

The limit of detection (LOD) and limit of quantification (LOQ) were determined according to the following formula:

LOD=3. 3 X SDa / b

LOQ=10 X SDa / b

Where: SDa is standard deviation of intercept, b is the slope. The LOD and LOQ were found to be 0.12 µg/mL and 0.36 µg/mL, respectively, Table 1.

Precision: The precision of the proposed method was determined by replicate analysis of three separate solutions of working standard at different concentration levels. The method gave satisfactory results; RSD did not exceed 2% indicating the good precision for the proposed method. This precision level obtained reflecting the usefulness of this method in routine analysis of the oxyfluorfen in laboratories.

Recovery: The accuracy and validity of the proposed method was evaluated by the recovery studies for added concentrations. The recovery of each was calculated as the amount found / amount taken X 100. The results of analysis suggest that there is no interference from any excipients, which are present in formulation Table 2.

Robustness: Robustness was examined by evaluating the influence of small variation in the method variables on its analytical performance. In this experiment, one parameter was changed whereas the others were kept unchanged, and the recovery percentage was calculated each time. It was found that small variation in the method variables did not significantly affect the procedures; recovery values were recorded in Table 3. This indicated the reliability of the proposed method in application for the analysis of oxyfluorfen.

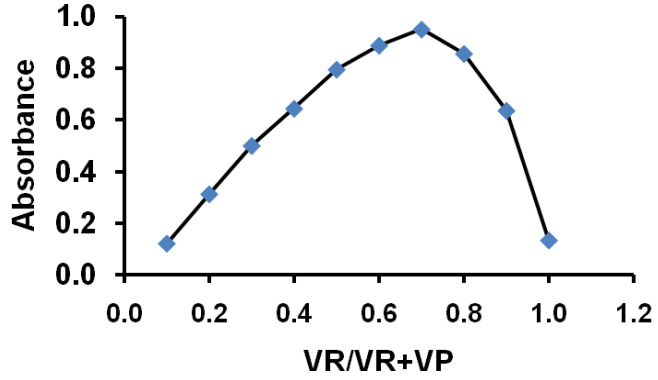


Figure 5: Determination of the product formation by Job's method. V_R: NQS (1.5×10^{-2} M); V_P: Oxyfluorfen (1.5×10^{-2} M); V_R+V_P=10 mL; total volume of reaction solution 11.5 mL.

Parameter	Value
λ_{max}, nm (pesticide)	285
λ_{max}, nm (product)	460
Beer's law limits, (µg/mL)	0.4-4.0
Molar absorptivity, l/moL cm	1.33×10^5
Sandell sensitivity, µg/cm^2	0.0027
Limit of detection , (LOD), µg/mL	0.12
Limit of quantification (LOQ), µg/mL	0.36
Regression equation,Y:*	**Value**
Intercept (a)	0.0906
Standard deviation of the intercept (SDa)	0.0094
Slope (b)	0.2579
Standard deviation of the slope (SD_b)	0.0038
Correlation coefficient (r^2)	0.9993

Table 1: Parameters for the performance of the proposed method. *Y= a+bX, where Y is the absorbance, a intercept, b slope and X concentration in µg/ml.

oxyfluorfen taken (µg/mL)	oxyfluorfen added (µg/mL)	oxyfluorfen found (µg/mL)	Recovery (% ± SD)*
1.0	1.0	1.87	93.50 ± 0.01
1.0	2.0	3.09	103.00 ± 0.01
1.0	3.0	3.77	94.25 ± 0.02

Table 2: The precision of the proposed method. *Recovery was calculated as the amount found/amount taken × 100. Values are mean ± SD: Standard Deviation. Mean values of three determinations.

Application of the proposed method to analysis oxyfluorfen residues in water, tomato fruits and Onion

The procedure was applied successfully to the determination of the oxyfluorfen residues in water, tomato fruit and onion. The results were listed in Table 4 are indicate the applicability of the procedure to analysis food and environmental samples containing oxyfluorfen pesticide with simplicity and high accuracy. The recovery of oxyfluorfen varied from 93.33-106.67% (Table 4).

Effect of washing and boiling on decreasing the oxyflourfen residues on tomato and onion samples

The percentage decreasing of oxyflourfen residues on tomato and onion samples, after boiling and washing are presented in Table 5, respectively. To determine the decreasing % of pesticide in spiked samples, after washing and boiling process each wash or boil treat sample concentration was compared to the untreated sample concentration. In the untreated samples, the concentration of oxyflourfen was 2.0 ppm. The results show washing three times reduced the residues by 46.5% in onion, 50% in tomato and boiling reduced the residues by 60.4 in onion, 81.15% in tomato. Boiling of tomato and onion was found to be more effective than washing in dislodging the residues.

Conclusion

The present study described the successful evaluation of NQS in the development of simple and rapid spectrophotometric method for the accurate determination of oxyfluorfen residues.

The proposed method is superior to the previously reported methods for the determination of oxyfluorfen in term of its simplicity. Furthermore, it does not need expensive instruments, have excellent

Parameters	Recovery (% ± SD)[a]
Recommended conditions	101 ± 0.85
Buffer solution (pH) 13.2 12.8	 104.98 ± 0.50 96.63 ± 0.38
Volume of NQS (mL) 2.2 1.8	 103.65 ± 0.43 97.52 ± 0.89
Temperature (^{0}C) 35 25	 99.13 ± 0.47 105.58 ± 0.39
Reaction time (min) 25 15	 104.64 ± 1.05 105.72 ± 0.45
Volume of buffer solution (mL) 2.2 1.8	 99.36 ± 0.66 97.74 ± 0.39
NQS concentration (w/v %) 0.55 0.45	 95.34 ± 0.13 96.75 ± 0.01

Table 3: Influence of small variations in the assay conditions on the analytical performance of the proposed spectrophotometric method for determination of Oxyfluorfen using NQS reagent. [a] Values are mean of 3 determinations.

Sample	Amount added (µg/mL)	Amount found (µg/mL)	Recovery (% ± SD*)
Water [a]	1 2 3	1.05 1.97 2.80	105.00 ± 0.59 98.5 ± 0.68 93.33 ± 0.12
Tomato [b]	2 3	2.08 3.11	104 ± 0.84 103.67 ± 1.24
Onion [b]	2 3	1.99 3.20	99.5 ± 1.26 106.67 ± 0.95

Table 4: Determination of Oxyfluorfen residues in water, tomato fruits and onion. *Average of three replicate analysis. [a]Amount of water sample=10 mL. [b]Weight of tomato and onion sample=50 g.

Type of sample	Residues in untreated* µg/ml ± RSD	Residues after Boiling µg/mL ± RSD	% Decreasing after Boiling	Three times washing* µg/mL ± RSD	% decreasing after three times washing
Tomato[a]	2.0 ± 0.56	0.377 ± 1.7	81.15	1.00 ± 3.45	50.0
Onion[a]	2.0 ± 0.91	0.792 ± 1.42	60.40	1.07 ± 2.87	46.5

Table 5: The decreasing (%) of OXY in Tomato and Onion after three times washing and boiling samples. *Average of five replicate analysis. [a]Weight of tomato and onion sample=50 g.

shell life, all the analytical reagents are inexpensive, are available in any analytical laboratory.

The other advantages include that, the method involves the measurement of stable colored species, have shorter contact time and they are free from the extraction step. Therefore, the method is practical and valuable for routine application in laboratories for the analysis of oxyfluorfen residues in food and environmental samples.

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