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DEVELOPMENT AND VALIDATION OF KINETIC SPECTROPHOTOMETRIC METHOD FOR HERBICIDE BROMFENOXIM DETERMINATION

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Abstract. *A kinetic spectrophotometric method for determining the residues of herbicide bromofenoxim (BrFX) has been developed and validated. The proposed method is based on the inhibitory effect of BrFX on the oxidation of sulfanilic acid (SA) by hydrogen peroxide in the presence of Cu(II) ion, which was monitored at 370 nm. The variables affecting the rate of the reaction were investigated and the optimum conditions were established. BrFX can be measured in the range of 0.041 – 0.46 μg/ml and 0.46 – 13.86 μg/ml. The detection limit of the method with 3σ criteria is 0.0077 μg/ml. The relative standard deviations for five replicate determinations of 0.041, 0.24 and 0.46 μg/ml BrFX are 3.0, 5.32 and 2.85%, respectively. This method can be successfully used to determine BrFX concentration in baby juice samples. The HPLC method is used to verify the results. The results obtained for the same samples by the two methods are quite comparable.*

Key words: *kinetic method, bromofenoxim, HPLC method, SPE, baby juice samples*

1. INTRODUCTION

Pesticides are substances (natural or synthetic) or a mixture of substances intended for preventing, destroying, repelling, or mitigating any pest (insects, weeds, diseases, fungi, bacteria, etc.) in order to obtain higher yields of agricultural crops, as well as to keep them safe while in storage. Phenoxy herbicides have been most widely used for controlling the growth of weed and other vegetation. They are relatively cheap and very efficient even at low concentration; therefore, they are extensively applied against grass and broad leaf

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Dedicated to Professor Radosav Palić on the occasion of his 70th birthday.
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weeds in many cereal crops. Due to their strong polarity, they can easily dissolve and diffuse in waters.

Herbicide bromofenoxim (Fig. 1) (3,5-dibromo-4-hydroxybenzaldehyde 2,4-dinitrophenyloxime) is used for the post-emergence control of annual broad-leaved weeds in cereals, maize grass seed crops, grassland and newly-seeded turf. BrFX is a foliar-applied contact herbicide absorbed by the leaves and stems with some limited translocation.

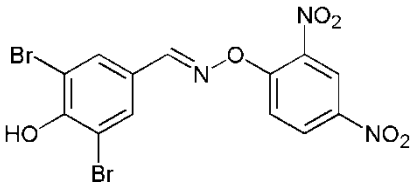

Fig. 1 Chemical structure of bromofenoxim (*E*-isomer shown)

Bromofenoxim belongs to the group of phenoxy herbicides, which are uncouplers of oxidative phosphorylation. These herbicides act as inhibitors of energy metabolism in plants. This property is also reflected in their acute mammalian toxicity which is higher than the range usually encountered with herbicides (100-300 mg/kg). The presence of pesticides in the environment has caused a great social and scientific concern. Traditionally, determination of trace levels of pesticide residues in aqueous samples relies on the use of liquid-liquid extraction (LLE) and solid –phase extraction (SPE).

Multi-residue methods for bromofenoxim determination have been reported by different authors. They used the gas chromatography (GC) (Eisert et al., 1995) for bromofenoxim determination in water. Liquid chromatography (LC) (Rosales-Conrado et al., 2005; (Chen et al., 2006; Lui et al., 2007) and capillary electrophoresis (CE) (Fu et al., 2009; Li and Cai, 2008; Li et al., 2009; Wen et al., 2012) have been widely used for separation and determination of phenoxy herbicides. Phenoxy herbicides have been determined by GC-MS after microextraction (Nuhu et al., 2012), and by LC/MS/MS (Santilio et al., 2009). Karlhuber et al., (1975) determined the bromofenoxim in hops by GC with mass fragmentation. Multi-residual method was developed for bromofenoxim determination in fatty food and non-fatty food in the interval of concentration 20 - 200 ppb (Hopper et al., 1992).

HPLC method has been used for phenoxy herbicide determination after extracting a solvent (Farhadi et al., 2009). A very sensitive HPLC method for the determination of bromofenoxim and its metabolite with hydroxyl groups has been developed by Faller et al. (1996). The sensitivity of the method is the order of picograms. Flanagan et al. (1989) determined the bromofenoxim in blood, plasma, serum and urine with a limit of quantitation of 10 mg/dm^3 and a relative error smaller than 8%. So far, a number of classic extraction methods such as liquid-liquid extraction (LLE) (Hiemstra and deKok, 2007), solid-phase extraction (SPE) (Rosales-Conrado et al., 2005) liquid-liquid-liquid microextraction (LLLME) (Chen et al., 2006; Melwanki and Huang, 2006; Wu et al., 2005) and dispersive liquid-liquid microextraction (DLLME) (Farhadi et al., 2009; (Yanling et al., 2013; Ma et al., 2012; Moreno-González et al., 2012; Lin et al., 2011) have been developed for sample pretreatment of phenoxy herbicides.

A number of analytical methods have previously been reported for the determination of BrFX in various matrices. However, as far as we know, there is no kinetic-spectrophotometric method for the BrFX determination in the literature.

The aim of our study was to develop a new kinetic-spectrophotometric method for BrFX determination and to apply the kinetic method for BrFX determination in baby juice samples after SPE.

2. EXPERIMENTAL

2.1. Reagents and chemicals

Bromofenoxim standard was obtained from Dr Ehrenstorfer (Germany) with a certified purity of 99%. Sulfanilic acid solution was prepared by dissolving a Merck 0.3463 g of SA in water (50 cm^3) in a standard flask.

The initial 2 mol/dm^3 solution of hydrogen peroxide was prepared from 30% H_2O_2 (Merck), and its exact concentration was standardized permanganometrically. Because of its limited stability, it was prepared just before use. A solution of Cu(II) $1 \cdot 10^{-3}$ mol/dm^3 was prepared by dissolving $CuCl_2 \cdot 2H_2O$ (Merck) in water. The phosphate buffer (Lurie, 1989) pH 7.9 was obtained by mixing solutions of KH_2PO_4 (0.067 mol/dm^3) and Na_2HPO_4 (0.067 mol/dm^3). Acetonitrile (ACN) and methanol (MeOH) was HPLC grade (Baker, UK).

Analytical grade chemicals and deionised water (MicroMed high purity water system TKA Wasseraufbereitungssysteme GmbH) were used for the preparation of all solutions. All the glassware used was washed with aqueous HCl (1:1) and then thoroughly rinsed with distilled water, and then finally with deionised water.

2.2. Apparatus

The reaction rate was monitored spectrophotometrically by measuring the rate of change of absorbance at 370 nm. The readings were performed on a Perkin-Elmer Lambda 15 UV/Vis spectrophotometer with 10-cm quartz cell pairs, connected to a thermo-circulating bath.

Chromatographic analyses were performed with an Agilent Technologies, Series 1200 liquid chromatograph, equipped-with an Agilent photodiode array detector (DAD), Model 1200 with RFID tracking technology for flow cells and a UV lamp, an automatic injector and Chem Station software. The analytical column was an Agilent – Eclipse XDBC-18 C18 column (250 × 4.6 mm). A model BÜCHI R-200/205 rotary vacuum evaporator including bath B-490 with a vacuum pump was used to evaporate the extracts.

Hanna pH-meter instrument was used for checking the pH measurements.

A J. T. Baker Model SPE-12 with a vacuum pump was used for solid phase extraction of samples.

In addition, high precision volume micropipettes (Lab Mate$^+$) of 50, 500 and 1000 μl were used for handling or pipetting the solutions.

The solutions were thermostatted at 25 ± 0.1 C º before the beginning of the reaction.

2.3. Procedure

In a four-compartment reaction vessel reactants were placed: 0.15 cm^3 of SA (0.04 mol/dm^3) in one compartment, 1 cm^3 H_2O_2 (2.0 mol/dm^3) in the second, 5 cm^3 phosphate buffer (pH 7.9) in the third, 0.4 cm^3 Cu^{2+} ($1 \cdot 10^{-4}$ mol/dm^3) and 1.0 cm^3 BrFX (138.6 μg/cm^3) in the fourth compartment and water was added to the total volume of 10 cm^3 and placed in a 25°C water bath. After the components had been brought to the

reaction temperature and mixed by vigorous shaking, the reaction mixture was transferred into a 10-cm temperature controlled cell in the spectrophotometer. The change in absorbance (A) at 370 nm as a function of time (t) was measured every 30 sec over a period of 6 min. The initial rate of the reaction at different concentrations of each of the reactants was obtained by measuring the slope of the linear part of the kinetic curves to the absorbance-time plot: from Beer's law $A = \varepsilon \cdot l \cdot c$; $dA/dt = \varepsilon \cdot l \cdot (dc/dt)$; slope = dA/dt; rate = dc/dt ; $dc/dt = (dA/dt)/\varepsilon \cdot l$. The calibration graph was constructed by plotting the slope of the linear part of the kinetic curve, versus concentration of the bromofenoxim (c_{BrFX} , μg/cm^3).

2.4. Juice sample preparation

Commercially available apple, peach, orange and blueberry juices were used for the optimization and validation of the analytical method. Fruit juice samples used for recovery studies were previously tested and proven to be free from the pesticide considered. For the real sample analysis, baby fruit juices of different brands produced by different domestic companies were purchased in local supermarkets and analyzed for pesticide residues. All juice samples were preserved at 4 °C.

Spiked juice samples for recovery determination were prepared by addition of appropriate amount of standard stock solution (0.2 mg/cm^3) and stay for 1 day. A 20 cm^3 volume of ACN was added, and the mixture was homogenized for 1 min, after centrifuging at 4000 rpm for 5 min. The organic phase was decanted into a graduated flask, and the volume of the extract was measured. SPE with Chromabond® HR-P cartridge was used for extraction of BrFX. Each sample solution was poured into a Chromabond HR-P cartridge (sorbent mass 200 mg Macherey-Nagel, Germany) which was conditioned with 10 cm^3 ACN, then 2 cm^3 deionised water, then water was filtered through the column, and the column was dried for 30 min under the gentle nitrogen steam. The sample was eluted with 2x5 cm^3 ACN and 5 cm^3 H_2O and then the extract was collected and evaporated at 40 °C in a rotary vacuum evaporator till dryness. The residue was dissolved with ACN, transferred into the volumetric flask (10 cm^3), made up with mobile phase (ACN-H_2O 80:20, v/v + H_3PO_4 0.5%) to the final volume of 10 cm^3 and filtered through Millipore membrane Teflon filters (0.45μm particle size) before injection into the chromatographic system. An equivalent of 10 μl was injected into the HPLC system. For kinetic determination 10 cm^3 of this solution was taken and evaporated at temperature of 40 °C till dryness, the residue was dissolved in MeOH, transferred in the 10 cm^3 volumetric flask and made up with water to obtain a solution the expected BrFX concentration of which was 200 μg/cm^3. This solution was reconstructed and used for kinetic determination. The mobile phase for the HPLC method consisted of ACN-H_2O (80:20,v/v) and the flow rate was 1 cm^3/min.

3. Results and Discussion

During the oxidation of SA by hydrogen peroxide in the presence of Cu^{2+} as a catalyst, a yellow colored reaction product was yielded, which exhibits an absorption maximum at 370 nm. In the presence of small amounts of BrFX in the system, the reaction was inhibited. The influence of the reaction variables (reagent concentrations, acidity) on the reaction rates was studied to establish the optimum reaction conditions. The system was optimized by altering each variable in turn, while the others were kept constant.

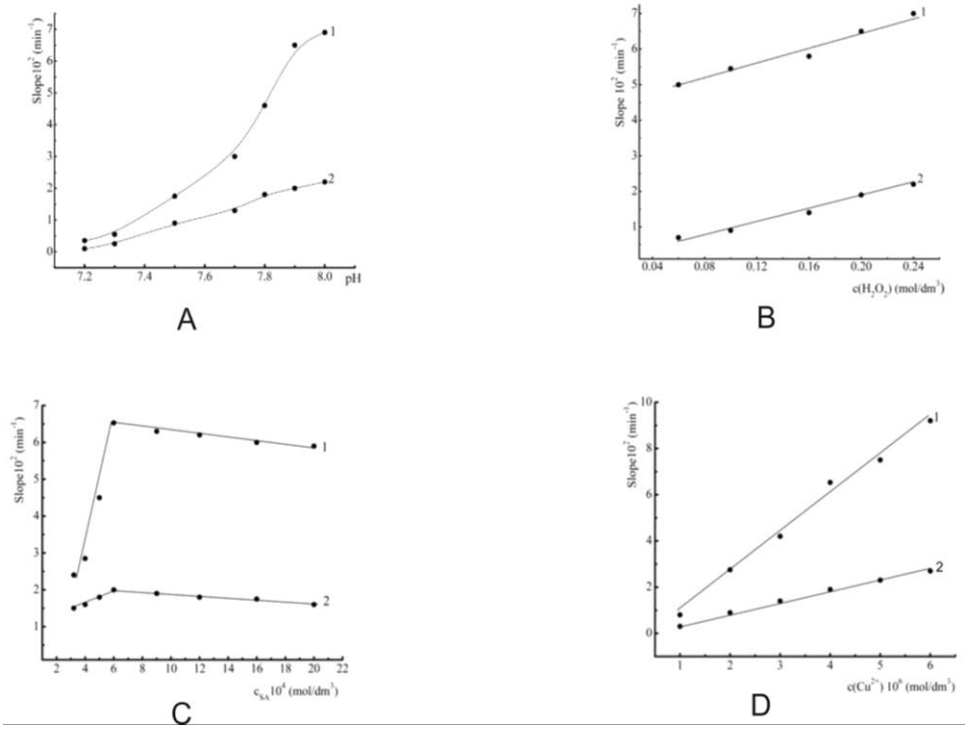

Fig. 2 Dependence of the reaction rate on: A) pH; B) hydrogen peroxide concentration; C) sulfanilic acid concentration; D) Cu(II) ion concentration for the catalyzed (1) and inhibited (2) reaction.

3.1. Kinetic studies

For the determination of BrFX in the concentration interval studied, the tangent method was chosen. The rate of the reaction was obtained by measuring the slope of the linear part of the kinetic curves of the Absorbance-time plot (slope = dA/dt). The effect of the acidity on the catalytic and inhibited reactions was studied (Fig.2.A). The pH was studied in the interval from 7.2 to 8.0. For further work a pH of 7.9 was selected. The effect of H_2O_2 on the rates of reactions was studied in the range 0.06-0.24 mol/dm^3. H_2O_2 concentration of 0.2 mol/dm^3 was chosen as optimal (Fig.2.B). The effect of SA concentration was studied in the interval $3.2 \cdot 10^{-4}$- $20 \cdot 10^{-4}$ mol/dm^3. For further work SA concentration of $6 \cdot 10^{-4}$ mol/dm^3 was chosen (Fig.2.C). The influence of Cu^{2+} concentration on the catalyzed and inhibited reactions was examined in the range $1 \cdot 10^{-6}$ - $3 \cdot 10^{-5}$ mol/dm^3. A concentration of $4 \cdot 10^{-6}$ mol/dm^3 was chosen as optimal (Fig.2.D)

Under the optimum experimental conditions: pH=7.9; c(H_2O_2) = 0.2 mol/dm^3; c(SA) = $6 \cdot 10^{-4}$ mol/dm^3; c(Cu^{2+}) = $4 \cdot 10^{-6}$ mol/dm^3, t = 25±0.1°C, linear calibration graphs were obtained by the tangent method of 6 min from the initiation of the reaction. It can be used for the determination of BrFX concentration in the interval 0.041 to 0.46 μg/cm^3 and from 0.46 to 13.86 μg/cm^3. During the examination of the inhibited effect of bromofenoxim on the reaction rate, it was determined that the kinetic curve is not linear in all investigated

intervals of bromofenoxim concentration. The breaking of the kinetic curve was determined in the bromofenoxim concentration of 0.46 μg/cm^3. Two kinetic curves with different slopes were constructed, and in two different intervals of concentration. Because of this, the linearity was divided into two linear ranges: one calibration curve from 0.041 to 0.46 μg/cm^3, and the second from 0.46 to 13.86 μg/cm^3, respectively.

Figure 3 shows the calibration curve at the temperature of 25±0.1°C. It can be used for the determination of BrFX concentration in the interval 0.041 to 0.046 μg/cm^3. On the basis of the results of this kinetic investigation the kinetic equations were formulated:

$$\text{Rate} = k_1 \cdot c(H^+)^{-1.1} \cdot c(H_2O_2) \cdot c(SA) \cdot c(Cu^{2+}) \quad (1)$$

$$\text{Rate} = k_2 \cdot c(H^+)^{-1} \cdot c(H_2O_2) \cdot c(SA) \cdot c(Cu^{2+}) \cdot c(BrFX)^{-1} \quad (2)$$

where k_1 and k_2 are the rate constants of the catalyzed and inhibited reaction.

The least squares equation (y = bx + a, where *b* and *a* are the slope and intercept, respectively) for the calibration graph and correlation coefficient *r* (Miller, 1991) for the determination of BrFX in the concentration range 0.041-0.46 μg/cm^3 and 0.46-13.86 μg/cm^3 under the optimal reaction conditions were calculated:

$$\text{Slope} * 10^2 = -5.83 * c_{BrFX} + 4.534 \qquad r = -0.9995 \quad (3)$$

$$\text{Slope} * 10^2 = -0.0852 * c_{BrFX} + 3.10 \qquad r = -0.9979 \quad (4)$$

The limit of detection (LOD) and quantification (LOQ) (Motolla, 1998; Ermer, 2001; Thomsen, 2003) are 0.007 μg/cm^3 and 0.025 μg/cm^3.

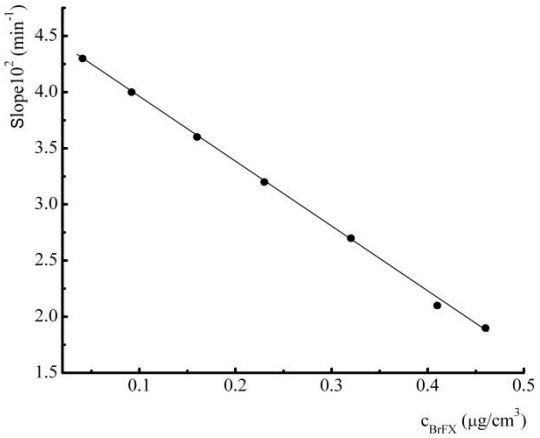

Fig. 3 Dependence of the reaction rate on the bromofenoxim concentration in the interval 0.041-0.46 μg/cm^3.

The precision and accuracy of the system were studied by performing the experiment five times for different concentrations of BrFX, and the results are presented in Table 1.

Table 1. Accuracy and precision of the bromofenoxim determination

Taken ($\mu g/cm^3$)	Found[a] $\overline{X}$ ±SD ($\mu g/cm^3$)	n	RSD (%)[b]	G (%)	$\frac{\bar{x}-\mu}{\mu}\cdot 100$ (%)[c]	Recovery (%)
0.041	0.037±0.001		3.0	1.34	9.75	90.24
0.24	0.23 ±0.01	5	5.32	2.37	4.16	95.83
0.46	0.45 ±0.01		2.85	1.4	2.22	97.82

[a]Mean and standard deviation of five determinations at 95 % confidence level;
[b]relative standard deviation; G- relative error; [c]accuracy of the method

3.2. Interference studies

To study the selectivity of the method, the effects of various cations and anions on the determination of 1.80 $\mu g/cm^3$ BrFX were studied. The tolerable concentration of each foreign ion was taken as the highest concentration causing an error of less than ± 5%. Most ions do not interfere with BrFX determination. Ions such as $Cu^{2+}$and Pb^{2+} interfere in all concentrations. Fe^{2+} and Fe^{3+} do not interfere when their concentrations are 10-times lower than the concentration of BrFX. V^{5+}, Al^{3+}, Cd^{2+} do not interfere when their concentrations are the same as the concentration of BrFX.

3.3. Applicability of the proposed method

The proposed method was applied to the determination of BrFX in baby juice samples using the direct calibration curve. As can be seen in Table 2, the results obtained for the kinetic method are in accordance with the HPLC method.

Table 2 shows that the F and t values at 95% confidence level are less than the theoretical ones, confirming no significant differences between the performance of the kinetic and HPLC method. Both recovery percentages and relative standard deviations (RSD) were satisfactory and indicated good performance of the proposed method for the analysis of bromofenoxim in fruit juice.

Table 2 Determination of bromfenoxim in baby juice samples by the kinetic and HPLC method

Juice sample	Added ($\mu g/cm^3$)	Kinetic method $\overline{X}$ ±SD ($\mu g/cm^3$)	RSD (%)	$\frac{\bar{x}-\mu}{\mu}\cdot 100$ (%)	Recovery (%)	HPLC $\overline{X}$ ±SD ($\mu g/cm^3$)	Recovery (%)	F value	t value
Apple HIPP	1.80	1.65±0.01	5.23	8.33	91.66	1.60±0.01	88.80	1.48	1.58
Apple Nectar	1.18	1.17±0.01	1.03	0.85	94.44	1.176±0.02	97.77	1.78	0.77
Cherry HIPP	3.60	3.38±0.03	1.20	6.50	93.88	3.43±0.01	95.28	1.95	2.15
Juice mix HIPP	0.25	0.23±0.03	1.62	8.02	92.00	0.241±0.01	96.40	1.19	1.50
Apple Nectar	0.20	0.191±0.02	1.93	4.52	95.52	0.196±0.02	98.22	3.12	1.65
Orange Juvitana	2.21	2.16±0.02	1.13	2.26	97.73	2.17±0.01	98.19	1.08	0.56
Blueberry HIPP	2.77	2.57±0.01	3.15	7.20	92.79	2.61±0.02	94.22	1.11	2.26
Carrot Juvitana	0.16	0.148±0.01	2.87	7.50	92.50	0.152±0.03	95.00	2.26	1.08
Peach HIPP	1.25	1.22±0.03	1.13	2.40	97.60	1.23±0.02	98.40	3.12	1.43
Pear HIPP	0.32	0.30±0.01	3.24	6.26	93.75	0.31±0.01	96.88	3.24	1.69

Figure 4 shows the chromatogram for BrFX determination in the spiked fruit juice sample for its concentration of 7.3 μg/cm^3 under the optimum conditions (ACN-water, 80:20, v/v + H_3PO_4; at a flow rate of 1 cm^3/min, and wavelength of 210 nm). The results of the proposed method were statistically compared with those of the parallel HPLC method using a point hypothesis test (Skoog et al., 1996).

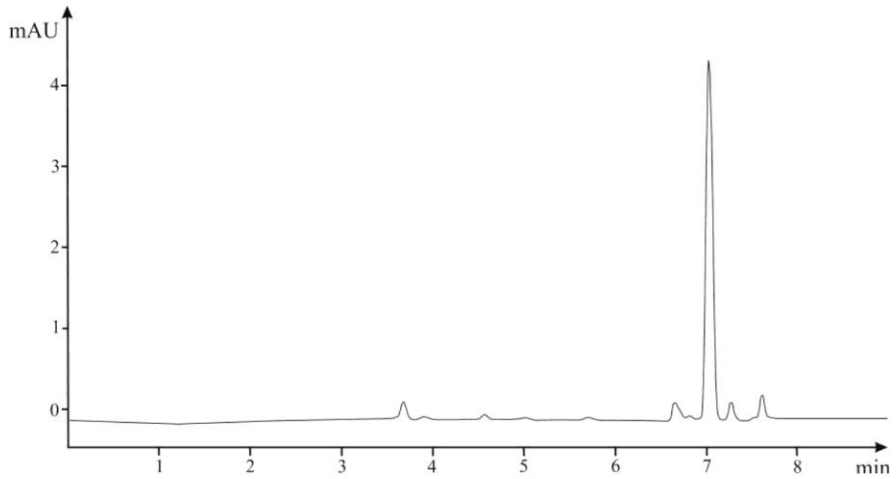

Fig. 4 HPLC chromatogram of the spiked juice sample with 3.60 μg/cm^3 bromofenoxim

4. CONCLUSION

A new reaction system was suggested for the kinetic spectrophotometric determination of bromofenoxim in baby juice. This method offers several distinct advantages, namely, high selectivity and sensitivity, cheap reagents, simple and inexpensive instruments, ease of operation, and rapidity. The statistical comparison of the results with the HPLC method showed a good agreement indicating no significant difference in accuracy and precision. Reliable recovery data were found at various concentrations, after spiking baby juice samples, and good limits of quantification were attained. The validity and simplicity of this method allows for the analysis of spiked baby juice samples with satisfactory results.

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RAZVOJ I VALIDACIJA KINETIČKO SPEKTROFOTOMETRIJSKE METODE ZA ODREĐIVANJE HERBICIDA BROMFENOKSIMA

Razvijena je i validirana kinetičko-spektrofotometrijska metoda za određivanje rezidua herbicida bromfenoksima (BrFX). Predložena metoda bazira se na inhibitornom dejstvu bromfenoksima u reakciji oksidacije sulfanilne kiseline vodonik peroksidom u prisustvu Cu(II jona) kao katalizatora. Merenja su vršena na talasnoj dužini od 370 nm. Određeni su optimalni eksperimentalni uslovi ispitivanjem uticaja svakog reagensa pojedinačno na brzinu indikatorske reakcije. Konstruisana je kalibraciona kriva u dva intervala koncentracija bromfenoksima od 0,041 do 0,46 μg/cm^3 i od 0,46 do 13.86 μg/cm^3. Granica detekcije metode prema 3σ kriterijumu je 0.0077 μg/cm^3. Određeni su optimalni eksperimentalni uslovi pri kojima BrFX pokazuje najjači inhibitorni efekat na indikatorsku reakciju. Postavljene su kinetičke jednačine za katalitički i katalitičko-inhibitorni proces. Relativna standardna devijacija (RSD) izračunata je za tri koncentracije BrFX 0,041, 0,24 i 0,46 μg/ml u pet ponavljanja i iznosi 3,0, 5,32 i 2,85%. Kinetičko-spektrofotometrijska metoda primenjena je za određivanje bromfenoksima u sokovima za bebe nakon ekstrakcije na čvrstoj fazi (SPE). Za potvrdu rezultata kinetičke metode rađena je HPLC analiza kao uporedna metoda. Obe metode su dale uporedive rezultate.

Ključne reči: *kinetička metoda, bromfenoksim, HPLC metoda, SPE, uzorci sokova za bebe*