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Solid surface fluorescence methodology for fast monitoring of 2,4-dichlorophenoxyacetic acid in seed samples

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ABSTRACT

A new method for pre-concentration/separation and determination of 2,4-dichlorophenoxyacetic acid (2,4-D) by solid-surface fluorescence (SSF) is proposed. The herbicide was complexed with Rhodamine B at pH 7.0 in the presence of phosphate buffer and anionic surfactant admicelles. A Nylon membrane was selected as a solid support for SSF measurement and the presence of 2,4-D was evident by the RhB quenching effect. Under optimal experimental conditions, the limit of detection and quantification were 6.93 and 21 ng L^{-1}, respectively, and the linear range was obtained from 0.021 to 22.11 μg L^{-1} 2,4-D concentration. The developed methodology showed good sensitivity and adequate selectivity, and it was applied to the 2,4-D determination in seed samples. The SSF represents a simple and fast alternative to conventional methods of analysis, employing an existing instrument in most laboratories.

1. Introduction

The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) is a synthetic analogue of the auxin hormone. Phenoxy herbicide compounds are currently among the most frequently used pesticides globally [1] as they provide broad-spectrum weed control at relatively low cost. It was promoted during World War II and first marketed in 1944. Currently, it is used in rice, corn, wheat, and in post-emergence applications in most developed countries.

In recent years, the hazards of using pesticides have been accentuated by an acute rise in agriculture. The inconvenience lies in the 2,4-D residues that end up contaminating aliments, soil and groundwater sources; workers who have occupationally handled it, also have been affected. An association between agricultural use of 2,4-D and the risk of non-Hodgkin's lymphoma has been demonstrated [2].

2,4-D has been classified as group 2B by the International Agency for Research in Cancer (IARC) due to the carcinogenic possibility to humans [3]. The World Health Organization (WHO) and U.S. Environmental Protection Agency (EPA) regulations have appointed a maximum contaminant level (MCL) of 10 to 70 ng mL^{-1} for chlorophenoxy acid herbicides in drinking waters [4,5]. Argentine legislation has established a maximum concentration level of 100 μg L^{-1} for total pesticides [6]. In some provinces like Chaco, Entre Ríos and Córdoba, 2,4-D aerial applications have been forbidden, and during the months of August to March, terrestrial applications have also been forbidden [7].

Diverse analytical methods have been proposed for the quantification of 2,4-D, including high performance liquid chromatography with UV–Vis detector, liquid chromatography coupled to mass spectrometry, [8,9] and capillary electrophoresis [10,11]. Procedures for the determination of herbicides include sample preparation most of the time as an obligatory step, particularly in the techniques for sample extraction, and extra-clean up prior to instrumental analysis. This previous step is time-consuming and involves the use of expensive instruments.

Luminescent methods are a combination of sensitive techniques which can detect changes in the local environment of the fluorophore employing an inexpensive instrument [12]. Its use is limited due to its moderate selectivity. The fluorescence measurement on a solid support where the analyte is isolated, can increase the selectivity, restricting the collisional deactivation and therefore improving the sensitivity; this strategy is named Solid Surface Fluorescence (SSF), and it has shown to be adequate and versatile in the treatment of samples of diverse nature [13–16].

As relatively few compounds are strongly luminescent, in some cases the analyte conversion into a luminescent compound is required through chemical complexation and/or photochemical reactions. Rhodamine B (RhB) is a highly water-soluble dye belonging to the methyxanthene family, with spectral luminescence properties. Because of this, it is employed as a pathological marker in lab testing and as a

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fluorescent water tracer. Some RhB derivatives have also been used as fluorescent chemosensors for metal ions [17–20].

Considering the adverse effects of 2,4-D on human health, the development of sensitive methodologies to monitor it at trace levels is relevant and necessary. In this research, an alternative methodology is proposed using an accessible instrument in control laboratories. To apply the new methodology for analyte determination in food samples, experimental parameters that impact the quality of analytical results will be studied and optimized.

2. Experimental

2.1. Reagents

A methanolic stock solution of 2,4-D (1×10^{-3} mol L^{-1}, Sigma-Aldrich, St. Louis, USA) was prepared by dissolving the appropriated amount. Further dilutions in ultrapure water were set up daily.

Stock solutions of Rhodamine B (1×10^{-3} mol L^{-1}, RhB-Fluka AG, Chemische Fabrik, Buchs SG, Switzerland) were prepared by dissolving the appropriate amount of reagent in ultrapure water. Further dilutions were prepared weekly in ultrapure water. The stability of solutions was checked by spectrophotometric measurements.

Buffer solutions (1×10^{-2} mol L^{-1}) of potassium dihydrophosphate (Biopack, Buenos Aires, Argentina), potassium biphthalate and sodium tetraborate (Mallinckrodt Chemical Works, New York, USA) and acetic/acetate (Mallinckrodt Chemical Works, New York, USA) were prepared, obtaining the desired pH by addition of dilute HCl (Merck, Darmstadt, Germany) or NaOH (Mallinckrodt Chemical Works).

Sodium dodecylsulfate (SDS), Triton® X-100 and hexadecyl trimethylammonium bromide (HTAB) were purchased from Tokyo Kasei Industries (Chuo-Ku, Tokyo, Japan).

All reagent used were analytical grade.

Nylon membranes (Millipore, Sao Paulo, Brazil) 0.45 μm pore size and 47 mm diameter, cellulose acetate (Whatman, England) 0.45 μm pore size and 47 mm, mixed esters (Schleicher & Schuell, Germany) 0.45 μm pore size and 47 mm, Immobilon (+) (Millipore, Sao Paulo, Brazil), Blue Ribbon filter papers (FP, Whatman, England) 2–5 μm pore size and 12.5 cm diameter were used as solid supports in sorption studies.

2.2. Apparatus

Spectrofluorimetric measurements were made using a Shimadzu RF-5301 PC spectrofluorometer equipped with a 150 W Xenon lamp and 1.00 cm quartz cells. For SSF measurements, a solid sample holder was used.

A combined glass electrode and a pH meter (Orion Expandable Ion Analyzer, Orion Research, Cambridge, MA, USA) Model EA 940 were used for pH adjustments.

2.3. Studied samples

A total of three different samples of flax, wheat and oats were purchased in local shops. Also, three different kinds of rice were acquired. The entirety of each product was homogenized and reserved for sample preparation. After that, 0.5 g of each seed was weighed and put in individual vials containing 10 mL of leaching solution (acetic acid, 1×10^{-3} mol L^{-1}), and they were continuously shaken for 5 min. Supernatants were separated and a general procedure was applied to a 25 μL aliquot of each leached solution [21–23].

2.4. General procedure

Adequate volumes of sample/standard solutions containing 2,4-D (0.021–22.11 μg L^{-1}), 500 μL RhB (1×10^{-6} mol L^{-1}), 500 μL buffer phosphate solution (1×10^{-3} mol L^{-1}, pH = 7.0) and 50 μL SDS (1×10^{-4} mol L^{-1}) were placed into a volumetric flask. The mixture was taken to 10 mL with ultrapure water. Systems were filtered across Nylon membranes, using a vacuum pump and were dried at room temperature. The 2,4-D concentration was determined on a Nylon membrane by SSF at $\lambda_{em} = 560$ nm ($\lambda_{exc} = 510$ nm; slit 3/3) using a solid sample holder (Fig. 1).

3. Results and discussion

3.1. Fluorophore nature and concentration

Because 2,4-D is a non-fluorescent compound, the use of a fluorophore is necessary for fluorescent detection. A variety of different

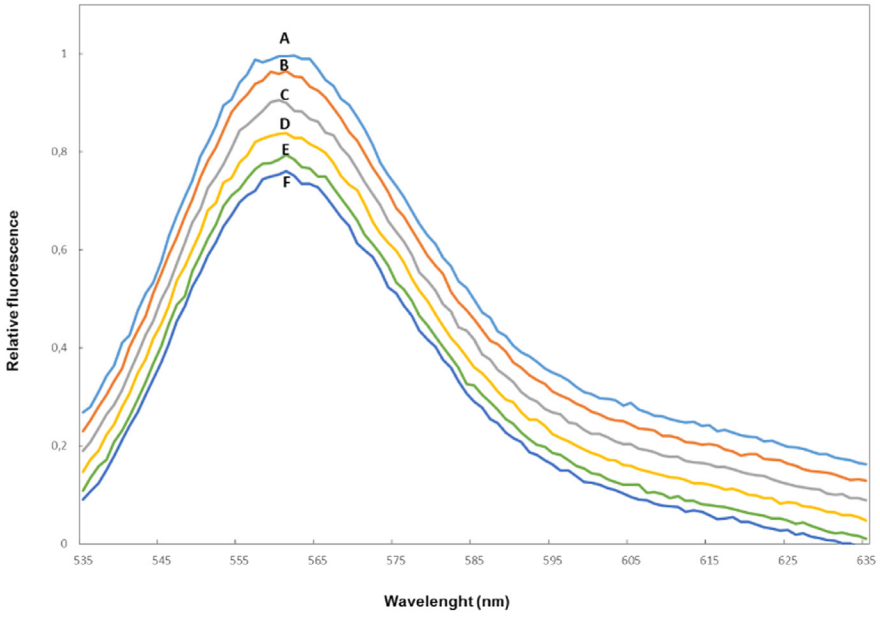

Fig. 1. Emission spectra of RhB/SDS and RhB/SDS-2,4-D systems. A: Nylon membrane with RhB ($C_{RhB} = 5 \times 10^{-8}$ mol L^{-1}) and SDS (1×10^{-4} mol L^{-1}); B: Idem A with 2,4-D 0.55 μg L^{-1}; C: Idem A with 2,4-D 1.10 μg L^{-1}; D: Idem A with 2,4-D 1.65 μg L^{-1}; E: Idem A with 2,4-D 2.20 μg L^{-1}; F: Idem A with 2,4-D 2.75 μg L^{-1} Conditions: $\lambda_{ex} = 510$ nm; $\lambda_{em} = 560$ nm; Slits 3/3; $C_{buffer\ phosphate} = 5 \times 10^{-3}$ mol L^{-1} (pH = 7).

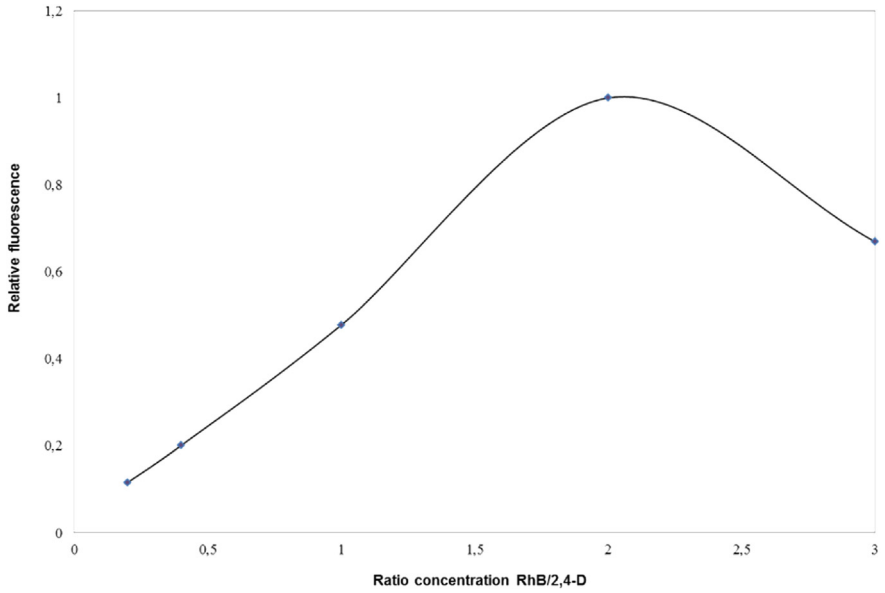

Fig. 2. Influence of RhB/2,4-D ratio on fluorescent emission. Conditions: $\lambda_{ex} = 510$ nm; $\lambda_{em} = 560$ nm; Slits 3/3; $C_{SDS} = 1 \times 10^{-4}$ mol L^{-1}; $C_{Buffer\ phosphate} = 5 \times 10^{-3}$ mol L^{-1} (pH = 7). Other experimental conditions are described under procedure.

fluorophores such as 8-hydroxyquinoline, dithizone, chromazurol S and Rhodamine B (RhB) were assayed. At the studied experimental conditions, no variation on native fluorescent response of fluorophores was observed. RhB showed a quenching effect only when 2,4-D was present; so this fluorophore was selected for optimization studies.

The RhB capability to form complexes with many organic species has been widely demonstrated [24–26]. In systems containing aromatic groups, such as nucleic acids, porphyrins, molecular clips, proteins and polymers, the molecular association involves a π-π interaction among aromatics rings of both compounds [27–30]. This interaction represents one of the principal non-covalent forces governing molecular recognition and biomolecular structure.

To improve sensitivity of the methodology, the fluorophore concentration must be optimized. Therefore, systems containing a constant concentration of 2,4-D and RhB concentrations from 2.5×10^{-9} to 7.5×10^{-8} mol L^{-1} were prepared and analyzed. The fluorescence signal was studied as function of the ratio RhB/2,4-D, as shown in the Fig. 2. A maximum intensity was obtained for a RhB/2,4-D ratio of 2. Using lower fluorophore concentration, the quenching effect is non-evident. When the dye concentration is increased to levels above 1×10^{-4} mol L^{-1}, self-aggregates are generated by π-π interactions inducing spectroscopic changes and affecting the dye photostability [31, 32]. An RhB concentration of 5×10^{-8} mol L^{-1} was established as the optimal concentration and was fixed for the following assays.

3.2. Surfactant concentration

It is well known that organized media provide enhancement of the sensitivity in fluorimetric determination, reducing the necessity of using organic solvent. The effect of surfactants SDS, Triton® X-100 and

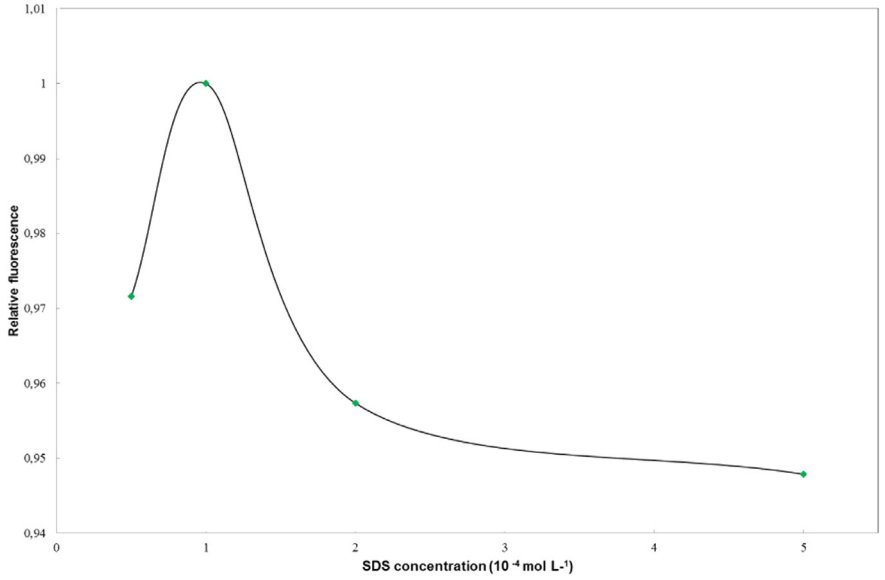

Fig. 3. Influence of SDS concentration on emission of RhB-2,4-D system. Conditions: $\lambda_{ex} = 510$ nm; $\lambda_{em} = 560$ nm; Slits 3/3; $C_{RhB}/C_{2,4\text{-}D} = 2$; $C_{Buffer\ phosphate} = 5 \times 10^{-3}$ mol L^{-1} (pH = 7). Other experimental conditions are described under procedure.

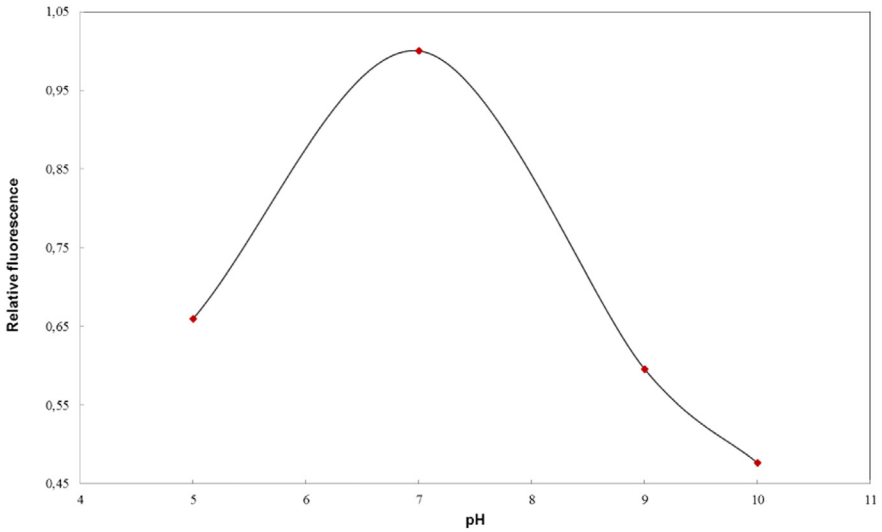

Fig. 4. Effect of pH on emission of RhB-2,4-D system. Conditions: $\lambda_{ex} = 510$ nm; $\lambda_{em} = 560$ nm; Slits 3/3; $C_{RhB}/C_{2,4\text{-}D} = 2$; $C_{SDS} = 1 \times 10^{-4}$ mol L^{-1}. Other experimental conditions are described under procedure.

HTAB on the RhB-2,4-D system was evaluated. For each tested surfactant, non-significant improvement in the quenching effect was achieved except for SDS. The anionic SDS improved the attenuation of the fluorescent signal of RhB-2,4-D complex.

To optimize the SDS concentration, systems were prepared varying the SDS concentration from 5×10^{-5} to 5×10^{-4} mol L^{-1}, keeping the RhB/2,4-D ratio constant at a value of 2. As shown in Fig. 3, the best quenching effect was achieved for an SDS concentration of 1×10^{-4} mol L^{-1} and it was chosen as the optimal concentration.

3.3. System pH, buffer nature and concentration

The system's pH has a direct influence on the capability of RhB to form complexes. RhB behaves as a zwitterionic molecule in a wide range of pH; in aqueous solution, many different forms characterized by typical absorption and fluorescent spectra can exist. Depending on the medium, pH, solvent presence, temperature and RhB concentration, the dye structures can include neutral form, molecular aggregates and ionized species [33]. On the other hand, a pKa value of 2.73 has been reported for 2,4-D [34].

The optimal pH value and buffer nature were evaluated using different buffer solutions: acetic acid/acetate (pH 5), phosphate (pH 7 and 9) and sodium tetraborate (pH 10). Other experimental parameters were kept constant with a RhB/2,4-D ratio of 2. The greatest sensitivity was achieved when the system was prepared at pH 7 using phosphate buffer (Fig. 4). At this pH value, 2,4-D is present as a negatively charged molecule and in this condition, it can interact electrostatically with the amino xanthene group of the RhB dye (positively charged).

To optimize the buffer concentration, systems containing phosphate solution from 1×10^{-4} to 1×10^{-2} mol L^{-1} (pH 7) were prepared. The maximum sensitivity was obtained for a phosphate concentration of 5×10^{-3} mol L^{-1}; for this reason, this concentration was chosen as optimal for the subsequent assays.

3.4. Solid support selection

The analysis of complex samples increases the probability of interference in the analyte determination, so a strategy of chemofiltration was implemented. Different solid supports were evaluated in sorption studies, including, Nylon membranes, cellulose acetate, mixed esters, Immobilon (+) and Blue Ribbon filter paper.

Systems were prepared at optimized experimental conditions containing a RhB/2,4-D ratio of 2 and were filtered through the solid supports. Filtered solutions were received in clean separated vessels; the solid supports were dried at room temperature. After that, they were placed in a solid sample holder and SSF was registered.

An adequate and selective retention of a RhB-2,4-D complex occurred when Nylon membranes were used; this support was chosen for analyte retention and the SSF determination. A quenching effect on RhB emission was produced in the presence of 2,4-D. Our research group has recently reported this quenching behavior for determination by SSF [35]. Also, filtered solutions were explored by molecular fluorescence; non-presence of RhB-2,4-D was evident, demonstrating the quantitative retention of the analyte on the Nylon membrane.

The filtration step allowed for the selective retention of the chelate containing the herbicide 2,4-D, separating it from a complex matrix sample. Furthermore, the solid support benefits from the planar configuration, which is energetically preferred in the excited state, and on the other hand, minimizes the vibrational deactivation processes.

4. Analytical figures of merit

Under optimal experimental conditions, the limit of detection (LOD) was determined as 3.3 times the standard deviation of the blank (N = 15) was 6.93×10^{-3} μg L^{-1}. The calibration plot is linear in the range of 0.021–22.11 μg L^{-1} for 2,4-D ($R^2 = 0.999$). Table 1 summarizes the

Table 1
Experimental conditions and analytical parameters for 2,4-D determination by SSF.

Parameter	Studied range	Optimal condition
Solid support	Cellulose acetate, nylon, teflon, filter paper	Nylon membrane
pH	5.0–10.0	7.0
Buffer potassium dihydrophosphate	1×10^{-4}–01×10^{-2} mol L^{-1}	5×10^{-3} mol L^{-1}
SDS concentration	5×10^{-5}–5×10^{-4} mol L^{-1}	1×10^{-4} mol L^{-1}
RhB concentration	2.5×10^{-9}–7.5×10^{-8} mol L^{-1}	5×10^{-8} mol L^{-1}
LOD	–	6.93×10^{-3} μg L^{-1}
LOQ	–	0.021 μg L^{-1}
Linearity range	–	0.021–22.11 μg L^{-1}
r^2	–	0.999

Table 2
Analytical parameters of methodologies for 2,4-D determination in different samples.

Method	Comments	Reference
FIIA	LOD = 0.05 μg/mL LOQ = 0.1 μg/mL Range linearity = 0.1–20 μg/mL $R^2 > 0.999$ Applied to drinking water	[36]
GC/MSD	LOQ = 5 μg L^{-1} Recovery = 79.3–98.2% Applied to human urine samples	[37]
RIA	Linearity Range = 1–200 μg L^{-1} Recovery = 92–98% $R^2 > 0.988$ Applied to urine samples	[38]
MEPIF	$R^2 > 0.996$ LOD = 72.2 μg L^{-1} Linearity range = 0.2–5 μg/mL Applied to water samples	[39]
This method	LOD = 6.93 × 10–3 μg L^{-1} LOQ = 0.021 μg L^{-1} Linearity range = 0.021–22.11 μg L^{-1} $R^2 = 0.999$ Recovery (%) = 97.22–103.07 Applied to seed samples	–

main characteristics of the calibration curve and optimized experimental conditions of the developed methodology; a comparative table (Table 2) shows the analytical parameters of the different methodologies for 2,4-D determination, highlighting the improvement in sensitivity achieved in the proposed new methodology.

5. Applications

The versatility of the proposed methodology was evaluated determining the analyte in seed samples. As it has been proven in previous studies, an acidic hydrolysis with acetic acid generates a significant enhancement of free 2,4-D [21]. Sample aliquots (25 μL) were spiked with increasing amounts of 2,4-D (0.55 and 1.10 μg L^{-1}), and the general procedure was applied. Reproducibility of the method was evaluated by 4 repetitions of the proposed methodology for each sample. Table 3 shows the recovery values obtained for each sample. The obtained results show satisfactory accuracy with adequate precision.

Table 3
Recuperation and validation studies by 2,4-D determination in different seed samples.

Sample	2,4-D added (μg L^{-1})	Proposed methodology	
		2,4-D found ± CV (μg L^{-1})	Recovery (%, N = 4)
1	–	0.78 ± 0.06	–
	0.55	1.35 ± 0.05	102.56
	1.10	1.87 ± 0.04	98.72
2	–	0.80 ± 0.03	–
	0.55	1.34 ± 0.05	98.75
	1.10	1.91 ± 0.09	101.25
3	–	0.61 ± 0.04	–
	0.55	1.17 ± 0.03	101.64
	1.10	1.70 ± 0.03	98.36
4	–	0.65 ± 0.08	–
	0.55	1.22 ± 0.01	103.07
	1.10	1.73 ± 0.02	96.93
5	–	0.87 ± 0.05	–
	0.55	1.42 ± 0.06	100.00
	1.10	1.95 ± 0.01	97.70
6	–	1.71 ± 0.08	–
	0.55	2.25 ± 0.03	99.42
	1.10	2.81 ± 0.09	100.00
7	–	0.72 ± 0.04	–
	0.55	1.25 ± 0.07	97.22
	1.10	1.83 ± 0.06	101.39

1 - Flax seeds.
2 - Wheat flour.
3 - Oat bran.
4 - Oat.
5 - Rice.
6 - Integral rice.
7 - Yamani rice.

6. Conclusions

The monitoring of pesticides in food samples is a matter of great importance due to health risks that its presence represents. The developed methodology provides a simple, economic, and fast procedure for 2,4-D monitoring in a variety of seeds available for human consumption, with an adequate precision. The selective retention and pre-concentration of 2,4-D on a Nylon membrane constitutes an interesting tool for its determination in studied samples. The implementation of a solid phase extraction strategy eliminates matrix effects from complex samples, allowing analyte quantification with recuperations near 100%. The developed methodology represents a compelling contribution for 2,4-D monitoring in food products to ensure healthy feeding.

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