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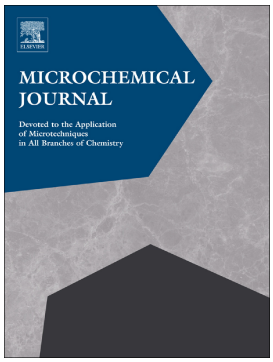

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PII: S0026-265X(17)31302-4
DOI: doi:10.1016/j.microc.2018.02.023
Reference: MICROC 3062

To appear in: *Microchemical Journal*

Received date: 19 December 2017
Accepted date: 19 February 2018

Please cite this article as: Magdalena Alesso, César A. Almeida, María C. Talio, Liliana P. Fernández , Metsulfuron-methyl determination in environmental samples by solid surface fluorescence. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Microc(2017), doi:10.1016/j.microc.2018.02.023

Metsulfuron-methyl determination in environmental samples by solid surface fluorescence

Magdalena Alesso, César A. Almeida, María C. Talio, Liliana P. Fernández*

INQUISAL- CONICET. Área de Química Analítica, Facultad de Química, Bioquímica y Farmacia. Universidad Nacional de San Luis. Chacabuco 917 (D5700BWS). San Luis, Argentina.

ABSTRACT

A new environmental friendly methodology for metsulfuron-methyl quantification based on the fluorescent signal enhancement of rhodamine B dye has been developed. A cationic surfactant (cetyltrimethylammonium bromide, CTAB) and an anionic one (sodium dodecylsulfate) were employed to preconcentrate the herbicide using a coacervation phenomenon, in sodium borate buffer medium (pH 9.2). The coacervate phase was collected on a nylon membrane (0.45 μm) and the solid surface fluorescence signal was determined (λ_{exc} = 515 nm, λ_{em} = 565 nm). Experimental variables that influence on preconcentration step and fluorimetric sensitivity have been studied and optimized using response surface methodology. Under optimal working conditions, a LOD of 0.17 μg L^{-1} and a LOQ 0.53 μg L^{-1} was obtained. The zeroth order regression calibration was linear from 0.53 to 5.00 μg L^{-1}. The method showed adequate sensitivity and selectivity, and was applied to the determination of trace amounts of metsulfuron-methyl in environmental water samples. The proposed methodology implies an alternative to traditional techniques for metsulfuron-methyl monitoring using an accessible instrument in control laboratories,

* Correspondence author

E-mail adress: lfernand@unsl.edu.ar (Dra. Liliana Fernández)
Phone: +54-0266-4425385.

representing a contribution in the toxicological and environmental areas for the monitoring of MSM in environmental samples, in agreement with the Green Chemistry.

Keywords: Metsulfuron-methyl; Herbicide; Fluorescence; Solid phase extraction

1. Introduction

Herbicides have been extensively used for decades and have substantially improved the food production. However, the unregulated and indiscriminate applications have generated an increased presence of residues in crops, soils and surface waters, affecting ground water and disrupting water treatment plants [1]. Their persistence is an important topic of concern due to adverse effects produced in human health, in different life forms and to the ecosystems in general [2].

The sulfonylurea herbicides are characterized by broad-spectrum weed control at very low rates (2-75 g ha^{-1}) showing good crop selectivity [3, 4] with systemic and residual action. This type of herbicides acts through inhibition of acetolactate synthase blocking the biosynthesis of the branched-chain amino acids like valine, leucine and isoleucine. This inhibition leads to the rapid cessation of plant cell division and growth [5].

Metsulfuron-methyl (MSM) is one of the most widely used herbicide from sulfonylurea family. It is mainly utilized to control a large variety of grass and broad-leaved weeds as pre-emergence application on wheat or as a post-emergence application on wheat, barley, flax, triticale and oat crops [6-8]. This herbicide is a labile and weakly acidic compound, with pKa= 3.8, indicating that urea nitrogens in this compound exist primarily in anion form in the environment. Under low pH conditions, it is hydrolyzed quickly; moreover, the microorganisms also play a significant role in the procedure of degradation. As a consequence of the poor chemical affinity among MSM and the agricultural soil (pH= 6.0

and above) this herbicide is only weakly adsorbed [9, 10] and is expected to biodegrade in soil from 27 to 60 days based on half-live time. It has the potential to leach under condition of high rainfall [11] and the residues can be found in aquifers and water sources that can be potentially used for human and animal consumption.

Due to the fact that water springs are sources of drinking water, many environmental agencies have introduced rigorous legislation regarding to guarantee the quality of those waters. In order to protect water systems, the European Union has established rigid limits for pesticides in water; in the case of surface waters that will be destined for human consumption, the limits are 1.0 μg L^{-1} for individual pesticides and 5.0 μg L^{-1} for the total of pesticides [12]. The low herbicide concentration employed in applications as well as the rapid degradation, results in a considerably low level of herbicide usually found in the environment. For this reason, it is important to develop rapid and simple methods with adequate sensitivity and selectivity to the determination of MSM residues at trace levels in complex matrixes [13, 14].

Different analytical methodologies have been proposed for the determination of MSM, such as high performance liquid chromatography [15-18], capillary electrophoresis [19, 20] and atomic force microscopy [21]. Likewise, spectrofluorometric methods are a combination of sensitive and selectivity techniques [22, 23], and previous researcher work have shown several analytical advantages in the application of molecular fluorescence in the determination of herbicides traces [24, 25]. However, previous investigations have demonstrated that MSM molecule does not show native fluorescence; so that, a prior step of photochemical degradation has been employed for the herbicides determination [26].

This paper reports an alternative method for the determination of Metsulfuron-methyl in river samples, using solid phase extraction (SPE) prior emission fluorescence detection. For

this purpose, the possibility of MSM complexion with Rhodamine B (RhB) was evaluated to achieve the fluorescent signal, thought a fluorescent complex.

2. Materials and methods

2.1. Reagents

Stock MSM solution 100 mg L^{-1} was prepared by dissolving Metsulfuron-methyl (Supelco, Bellefonte, P.A., USA) in methanol. Further dilutions 100 μg L^{-1} in methanol were weekly made. All solutions were protected against light with aluminum foil and kept in a refrigerator at 4 °C.

Stock solutions of Rhodamine B 1 mmol 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 weekly prepared in ultrapure water. The stability of solutions was checked by spectrophotometric measurements.

Buffer Tris 0.01 mol L^{-1} (Mallinckrodt Chemical Works, NY, USA), Potassium dihydrophosphate (Biopack, Buenos Aires, Argentina) buffer solution 0.01 mol L^{-1} biphthalate and tetraborate (Mallinckrodt Chemical Works) were used, obtaining the desired pH by addition of dilute HCl (Merck, Darmstadt, Germany) or NaOH (Mallinckrodt Chemical Works).

Sodium dodecylsulfate (SDS), hexadecyl trimethylammonium bromide (CTAB) were purchased from Tokyo Kasei Industries (Chuo-Ku, Tokyo, Japan).

All chemicals used were analytical grade and ultrapure water was used throughout.

The following solid supports were tested in sorption studies: 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 cellulose ester membrane filters (Schleicher

& Schuell, Germany) 0.45 μm pore size and 47 mm; Immobilon-FL® (Polyvinylidene difluoride membrane, Millipore, Sao Paulo, Brazil); filter papers Blue Ribbon (FP, Whatman, England) 2-5 μm pore size and 12.5 cm diameter.

2.2. Instrumentation

Fluorescence spectra were performed on Shimadzu RF-5301PC spectrofluorometer (Shimadzu Corporation, Analytical Instrument Division, Kyoto Japan) equipped with a 1.0 cm quartz cell and discharged Xenon lamp. The excitation and emission slits with a band pass of 1.5 / 3 nm were used for all measurements.

An Orion Expandable Ion Analyzer pHmeter (Orion Research, MA, USA) Model EA 940 with a combined glass electrode was used to carried out pH adjustments.

2.3 Sampling procedure

Water samples were collected in three different places of a river near to crop fields in the province of San Luis, Argentina. They were filtered, and analyzed following the proposed method. Samples were immediately refrigerated until processing.

2.4. General procedure

Adequate volumes of sample and/or standard solutions containing MSM (0.1-5 μg L^{-1}), 550 μL RhB 1 μmol L^{-1}, 500 μL buffer phosphate solution 0.02 mol L^{-1} (pH = 9.2), 200 μL SDS 0.02 mol L^{-1} and 650 μL CTAB 1 mmol L^{-1} were placed into a volumetric flask. The whole mixture was made to 4 mL with ultrapure water and place in a shaker for 10 minutes (1500 rpm). Systems were filtered through different solid supports, using a vacuum pump and dried at room temperature. The MSM concentration was determined on the supports by solid surface fluorescence at λ_{em} = 564 nm (λ_{exc} = 510 nm; slit 1.5/3) using a solid sample holder.

2.5 *Experimental design*

Preliminary experiments determined that the concentration of the fluorosphore, and concentration of each of the surfactants are the most important independent factors that affect the intensity of the fluorescent signal. The optimization of these parameters was performed using central composite design, where each numeric factor was varied over 5 levels (plus and minus alpha, axial point) plus and minus factor points, and the center point. The signal intensity was the dependent variable used to evaluate the methodology. The complete design consisted of 15 experimental runs. All data were processed using Design-Expert 7.0.

2.5. Accuracy and precision study

A volume of 1.5 mL of each sample was spiked with increasing MSM amounts (1.0, 2.5 µg L^{-1}). The repeatability (within-day precision) of the method was tested for replication of samples (n=7) spiked with the concentration mentioned above.

3. Results and discussion

3.1 Optimization of SPE experimental conditions for the determination of MSM

In the present work, the possibility of MSM complexion with fluorophores such as eosine, 8-hidroxiquinolein, rhodamine B and fluorescein were evaluated. However, in the presence of MSM, RhB was the only one fluorophore able to form a fluorescent complex.

It has been reported that RhB has different pH-dependent structures. Hence, pH in the solution has a direct implication in RhB molecule and the capability to complex formation with MSM. Also, self-aggregation of protonated RhB is described in the literature [27] which implies a diminution of fluorescence signal. Moreover, at pH below 5, the sulfonylurea induces the association/protonation of RhB and its spectral characteristics

change [28]. Thus, the pH value of the aqueous systems containing a constant concentration of both MSM and RhB was adjusted between 5 and 10 employing the following buffer solutions: potassium biphthalate (pH 4), acetic acid/sodium acetate (pH 5.3), Tris (pH 6), sodium biphosphate (pH 7) and sodium tetraborate (pH 9, 9.2, 9.5, 10). Best signal was achieving with sodium tetraborate buffer pH 9.2 (Fig. 1). Buffer concentration was optimized in the range 0.10 to 0.75 mmol L^{-1}. The best response was obtained with an optimal concentration of 0.25 mmol L^{-1}.

Figure 1

In order to improve the fluorescence intensity of de MSM-RhB complex, a previous coacervation step was carried out. It was shown a beneficial effect employing a cationic tensoactive forming a coacervate with an anionic one [29, 30]. In presence of polyelectrolytes, the concentration at which surfactant molecules start to form aggregates, critical aggregation concentration (CAC), is much lower than the CMC (critical micellar concentration) of the surfactant itself. Beyond CAC, small surfactant aggregates with lower aggregation numbers bind on the polyelectrolyte chains, forming necklace-bead complexes [31]. The complexes associate with each other, resulting in coacervation. With further adding the surfactant into the polyelectrolyte aqueous solution, coacervates may be re-dissolved by excess micelles [32]. In literature, plenty of studies have demonstrated the increasing in sensitivity and longer linearity range in micellar media if compared to that observed in homogenous solvents [33]. In condensed homogeneous media, the solvent molecules can participate in some excited-state evolution pathway. In organized media, the emitting excited state is protected from quenching by the micro-aggregate environment, consequently the observed emission intensities are usually many times greater than in the corresponding homogeneous media [31, 32].

In the present experimental research, with the aim of obtain the above mentioned important advantage, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were employed to form the coacervate. Both tensoactive concentrations were evaluated in preliminary studies and afterwards were optimized by an experimental design.

Other significant parameter to consider is the fluorophore concentration attending that RhB concentration must be sufficiently high to guarantee the MSM/RhB association and guarantee the quantitative formation of the complex. However, at concentrations over 0.1 mmol L^{-1} RhB molecules experiment self-aggregation by means of π-π interactions [27]. The aggregation induces spectroscopic changes and affects dye fluorescence-efficiency and photostability [34]. For that reason, to improved fluorescence signal, RhB concentration was optimized by an experimental design, with assayed levels in values from 0.5 to 1.2 μmol L^{-1}.

Solid phase extraction offers several advantages such as flexibility, higher enrichment factors, simplicity and safety. Moreover, previous works have demonstrated that the deposit of the coacervate on solid surface improve the limits of detection and avoids the drawbacks associated to compounds desorption [35-37]. Different types of solid supports were studies in the present work (Filter paper, cellulose acetate, mixed cellulose ester, Nylon and Immobilon-FL). Nylon membranes showed to be more suitable for the determination because of improvement of fluorescence signal and reproducibility.

Response surface methodology (RSM) was used to determine the optimal conditions for RhB, CTAB and SDS, obtaining a polynomial model to describe the relation between a response and the considered factors. The experiments were performed according to the central composite design given in Table 1, and quadratic equation for predicting the

optimum point was obtained. The concentrations of the solutions used are those mentioned in section 2.4.

Table 1

The relationship between the response (y) and the independent variables in the coded units results as follows in equation 1:

$$y = 519.41 + 73.77 * X_1 + 141.45 * X_2 + 167.25 * X_1 * X_2 + 69.18 * X_1 * X_3 \quad (1)$$
$$- 89.95 * X_1^2 - 114.80 * X_2^2$$

The results of the ANOVA for the quadratic equation were: R^2 = 0,971; Predicted R^2= 0.919; Adjusted R^2 = 0.973 and a coefficient of variation (CV) = 0.97 %. The Model F-value of 42.91 implies that the design was significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. The three-dimensional response surface plots are shown in figure 2 with fluorescence signal as the response.

Figure 2

It is noted that the fluorescence intensity increase with proportion of RhB, whilst SDS decrease the signal; however, the SDS is required for the coacervate formation. The best condition selected to work were with a volume of 650 µL RhB, 650 µL CTAB and 200 µL SDS corresponding to a concentration of 1.1 µmol L^{-1}, 1.6 mmol L^{-1} and 0.15 mmol L^{-1}, respectively.

3.1. Analytical figures of merit

The zeroth order regression calibration plot applying the developed methodology was linear for crescents MSM concentration levels from 0.53 to 5.00 µg L^{-1}. Table 2 summarizes the main characteristics of the calibration plot and optimized experimental conditions, which sustain the proposed procedure for quantification of MSM traces. The limits of detection

(LOD) and quantification (LOQ) were calculated according to the official compendia methods [35]. Using the relation k (SD) /m where k = 3.3 for LOD and 10 for LOQ. SD represents the standard deviation from 15 replicate blank responses and *m* is the slope of the calibration curve.

Table 2

3.2. Validation and applications

The proposed methodology was applied to determine MSM in natural water samples. MSM concentration was quantified in river-water samples by means of the standard addition procedure. Method validation was performed using procedures recommended in the Standard Methods for Examination of Water and Wastewater [38]. For this purpose, two river samples were spiked with different concentration of MSM. As additional information, conductivity and organic matter were analyzed. The values of electrical conductivity and chemical oxygen demand for river samples 1 and 2 were 279 and 1825 μS cm^{-1}, 1.12 and 7.89 mg O_2 L^{-1}, respectively.

Bias was studied by performing a recovery test at two concentration levels (1.0 and 2.5 μg L^{-1}). River water samples were prepared by spiking an appropriate amount of MSM, and were analyzed according to the optimized conditions (n= 6). The recovery values presented were good (between 98.1 % and 104.4 %) and they were obtained with suitable precision (Table 3).

The accuracy of the proposed method was evaluated in terms of repeatability (intraday precision). Repeatability was studied at two concentration levels, as the previous, for MSM using six replicate determinations for each concentration within one day. The mean and coefficient of variation (%CV) are shown in Table 3. All values were below 3.72 %, showing that the method is reliable for the analysis of MSM in studied samples.

Table 3

4. Conclusions

The proposed methodology represents an alternative to conventional methods of MSM quantification, contributing to environmental monitoring of herbicide contaminants. In this way, a simplification and lower operational cost is achieved with a suitable limit of detection. The solid phase extraction method was used for selective retention and preconcentration of MSM on Nylon membrane demonstrating to be a powerful tool for sensitive determination of the analyte in studied samples. The developed technique was validated using the standard addition method and applied to water samples with successfully results. Samples spiked with a known quantity of MSM were analyzed to demonstrate the absence of interferences. The methodology evidences good reproducibility with low operational cost. Among its vantages, it must be mentioned the generation of low amounts of waste, taking care of the analyst and the environment, as well. In this sense, it represents a contribution to green chemistry.

Acknowledgments

Authors gratefully acknowledge at Instituto de Química de San Luis–Consejo Nacional de Investigaciones Científicas y Tecnológicas (INQUISAL-CONICET Project PIP 112 201301 00605 CO) and Universidad Nacional de San Luis (Project PROICO 02-1016) for financial support.

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Figure caption

Figure 1. Effect of pH on the formation of fluorescent MSM-RhB complex.

Figure 2. Response surface plots for the best response of detector as a function of RhB, CTAB and SDS.

Table 1. Independent variables and their coded and actual values used for optimization.

Independent variable	Units	Symbol coded	Coded levels			
			-1	**1**	**-α**	**+α**
[a]RhB	µL	X_1	250	600	177	672
[b]CTAB	µL	X_2	400	800	317	882
[c]SDS	µL	X_3	200	400	158	441

Table 2. Experimental conditions and figures of merit.

PARAMETERS	STUDIED RANGE	OPTIMAL CONDITION
pH	5 – 10	9.22
Solid support	Filter paper, cellulose acetate, mixed cellulose ester, Nylon and Immobilon-FL.	Nylon
***RhB**	5.0 – 12 × 10^{-7} mol L^{-1}	11 ×10^{-7} mol L^{-1}
***SDS**	1.6- 3.2 × 10^{-3} mol L^{-1}	1.6 × 10^{-3} mol L^{-1}
***CTAB**	8.0 – 16 × 10^{-5} mol L^{-1}	15 × 10^{-5} mol L^{-1}
LOD	0.17 µg L^{-1}	
LOQ	0.53 µg L^{-1}	
Linear range	0.53 -5.00 µg L^{-1}	

*Total concentration in solution.

Table 3. Accuracy and precision for the analysis of MSM.

River sample	Nominal Value (µg L^{-1})	Added Value (µg L^{-1})	Found ± SD[a] (µg L^{-1})	Recovery [b] (%)	CV [c] (%)
1	0.84	1.00	1.82 ± 0.15	98.1	5.34
		2.50	3.36 ± 0.12	100.8	3.72
2	0.76	1.00	1.74 ± 0.11	98.4	4.11
		2.50	3.36 ± 0.03	104.4	3.78

[a] Mean ± standard deviation for six determinations.

[b] % Recovery = 100 * (analyte concentration in fortified sample – analyte concentration in the unfortified sample) / analyte concentration added in the unfortified sample.

[c] % Coefficient variation = (100 * SD/mean).

Highlights

- An alternative methodology for MSM quantification is proposed.
- Nylon membranes were used as a solid support for solid fluorescent determination.
- Experimental variables that influence were optimized by Response Surface Methodology.
- The methodology shows good reproducibility with low operation cost.
- Non-polluting solvents were used, preserving the analyst and the environment.
- It was applied to the determination of MSM in water samples.

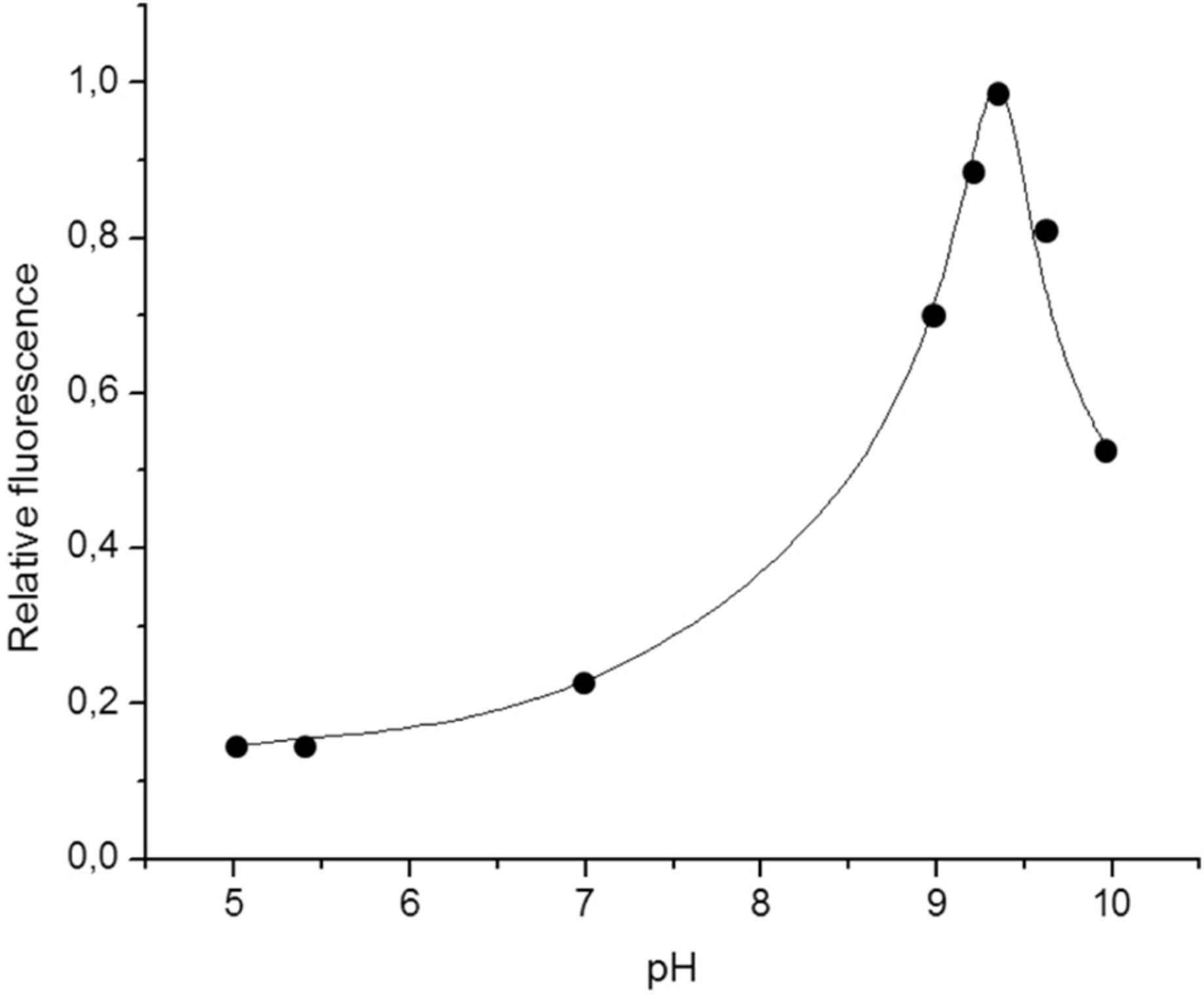

Figure 1

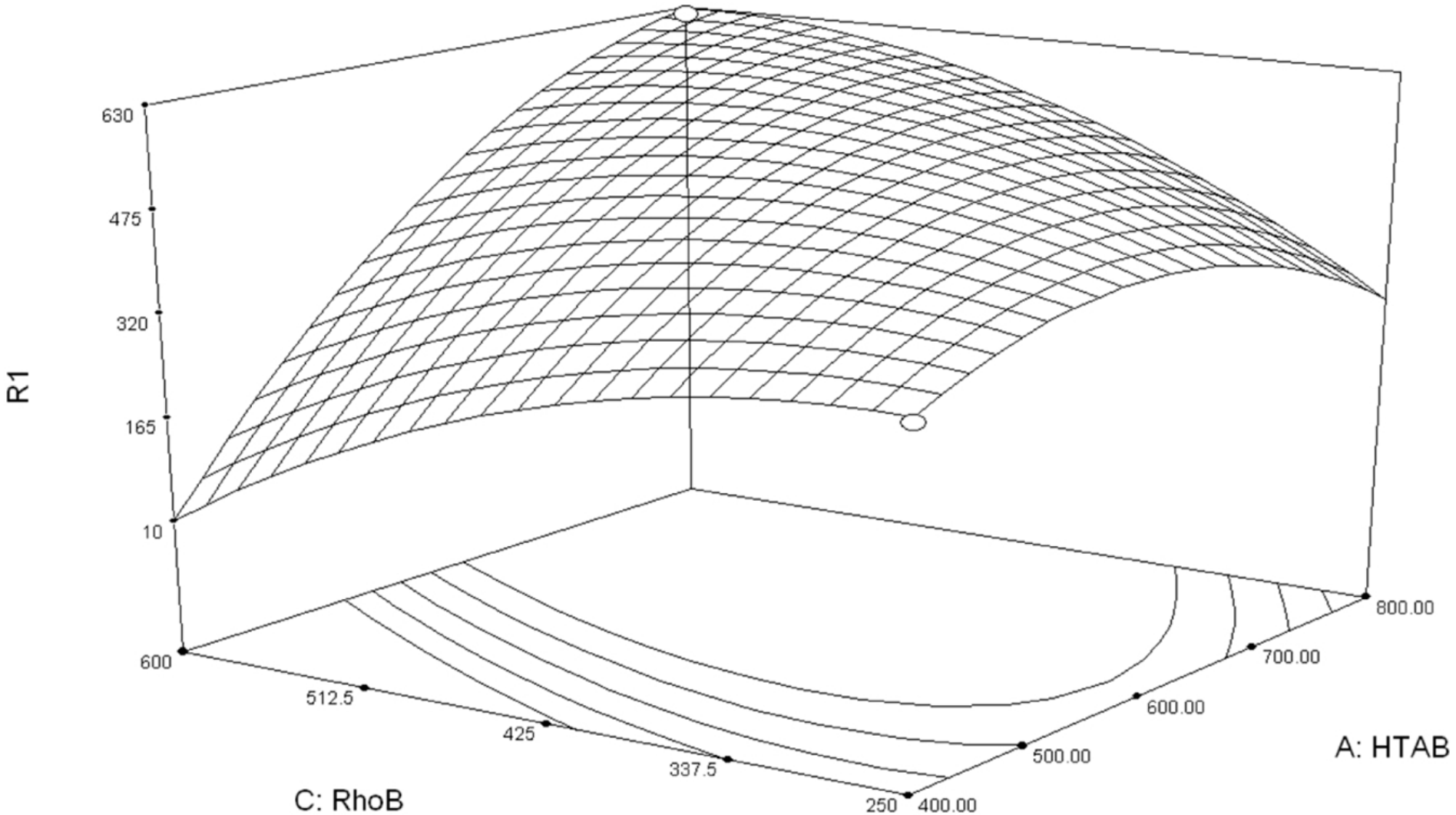
R1
630
475
320
165
10
600
512.5
425
337.5
250
C: RhoB
400.00
500.00
600.00
700.00
800.00
A: HTAB

Figure 2