# Supramolecular Solvent-Based Microextraction of Propachlor and Prometryn Herbicides in Soil Samples Prior to Liquid Chromatographic Analysis

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**Abstract.** Supramolecular solvents (SUPRASs) are the nano-structured liquids generated from amphiphiles through a self-assembly process, and constitute an alternative to molecular organic solvents with becoming more environmentally friendly in sample preparation step. In this study, a SUPRAS-based analytical method has been proposed for the microextraction of propachlor and prometryn herbicides in soil samples. The method involved the vortex mixing of the 300 mg of soil sample with 300 µL of SUPRAS for 8 min, subsequent centrifugation for the phase separation, and direct analysis of the SUPRAS phase by liquid chromatography with ultraviolet detection. Under optimal extraction conditions, the extraction recoveries for the herbicides ranged from 81 to 87 %. The method detection limits for propachlor and prometryn were 0.07 and 0.01 µg/g, respectively. Relative standard deviations obtained for the herbicides were less than 8.8 % and 12.1 % for intra-day and inter-day precisions, respectively. The microextraction of related herbicides from soil samples collected from the Zonguldak region was carried out efficiently. The recoveries obtained from spiked soil samples ranged from 80 to 108 %.

*Keywords*: Supramolecular solvent, microextraction, herbicides, soil samples, liquid chromatography.

## Toprak Örneklerindeki Propaklor ve Prometrin Herbisitlerinin Sıvı Kromatografisi Analizleri Öncesinde Supramoleküler Çözücü Esaslı Mikroekstraksiyonu

**Özet.** Supramoleküler çözücüler (SUPRASs), amfifillerin kendiliğinden bir birleşme prosesi ile meydana getirdiği nano yapılı sıvılardır ve örnek hazırlama basamağında daha çevre dostu olmaları nedeniyle moleküler organik çözücülere bir alternatif oluştururlar. Bu çalışmada, toprak örneklerindeki propaklor ve prometrin herbisitlerinin mikroekstraksiyonu için SUPRAS esaslı bir analitik metot önerilmektedir. Önerilen metot, 300 mg toprak numunesinin 300 µL SUPRAS ile 8 dakika boyunca vorteks ile karıştırılmasını, ardından faz ayrımı için santrifüjlemeyi ve ultraviyole dedektörlü sıvı kromatografisiyle SUPRAS fazının doğrudan analizini içermektedir. Optimize edilen ekstraksiyon koşullarında, herbisitler için ekstraksiyon verimleri % 81 ile % 87 arasında değişim göstermiştir. Metot algılama limitleri, propaklor ve prometrin için sırasıyla 0.07 µg/g ve 0.01 µg/g olarak bulunmuştur. Herbisitler için bulunan bağıl standart sapma değerleri gün-içi ve günler-arası tekrarlanabilirlik olarak sırasıyla % 8.8 ve % 12.1'den daha düşük bulunmuştur. İlgili herbisitlerin Zonguldak bölgesinden toplanan toprak örneklerinden mikroekstraksiyonu verimli bir şekilde yapılmıştır. Standart madde ilavesi yapılan toprak örnekleri için elde edilen geri kazanım değerleri %80 ile %108 arasında değişim göstermiştir.

*Anahtar Kelimeler*: Supramoleküler çözücü, mikroekstraksiyon, herbisitler, toprak örnekleri, sıvı kromatografisi.

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## 1. INTRODUCTION

Despite the significant technological advances in instrumental analysis methods over the last years, a sample preparation step prior to instrumental analysis for target analytes in some complex matrices (environmental, food, and biological) is still required. It enables the isolation and preconcentration of the analytes as well as the compatibility of the media with the instrumental system [1].

The solid sample treatment is commonly performed with conventional liquid solvent extraction techniques such as Soxhlet and ultrasonic extraction, which require long extraction times and the use of large volumes of frequently toxic organic solvents [2]. Some alternative extraction techniques such as microwave-assisted extraction [3], pressurized liquid extraction [4] and supercritical fluid extraction [5] have been developed and used for the extraction of organic analytes from solid samples. These techniques reduce the organic solvent consumption and extraction time but require expensive extraction equipment. In most cases, additional sample cleanup and solvent evaporation steps are necessary after the extraction, which might lead to analyte losses and lower extraction recoveries correspondingly. In the last few years, a great deal of interest has been focused on miniaturization of sample preparation processes with environmentally friendly solvents, including ionic liquids [6], deep eutectic solvents [7] and supramolecular solvents (SUPRASs) [8].

Alkyl carboxylic acids and alkanols are amphiphilic compounds consisting of both hydrophilic and hydrophobic groups. They are completely soluble in a solvent such as THF and form reverse micelles in the solution. The addition of water to the THF phase containing amphiphiles causes the spontaneous formation of amphiphile-rich phase, which was recently named as SUPRAS [8,9]. The density of SUPRAS is slightly lower than that of the bulk solution, which facilitates phase separation into two phases. The

microscopic analysis revealed that the amphiphilic molecules in the SUPRAS phase are exhibiting hexagonal structures [9]. They consist of aqueous cavities surrounded by the polar groups of alkanols with the hydrocarbon chains dissolved in THF. Increasing the THF/water ratio during the synthesis leads to the expansion of aqueous cavities in the hexagonal structure, which provides these solvents restricted access properties. These solvents can therefore extract low molecular weight analytes by hydrogen-bonding and hydrophobic interactions, while they can exclude macromolecules based on both size exclusion and precipitation mechanisms [10]. This feature improves the selectivity of the SUPRAS-based methods without the need for a clean-up step. Because SUPRASs provide multiple interaction sites for the target analytes in a wide polarity range, they have been successfully applied to the extraction of many organic analytes such as polycyclic aromatic hydrocarbons [10], bisphenols [11], curcuminoids [12], endocrine disruptors [13] and non-steroidal anti-inflammatory drugs [14] in very different environments.

Herbicides are the main group of pesticides used extensively in agricultural crop production to control the growth of different unwanted plants. Their transport into the food chain via contaminated soil can be considered a risk for human health due to the toxicity of most of these compounds [15]. Therefore, developing a rapid and efficient analytical method to monitor herbicides in soil samples is of particular importance. In the present study, an optimized and validated method for the determination of propachlor and prometryn herbicides in soil samples has been proposed. The analytes were isolated from the sample matrix using SUPRAS-based microextraction method and subsequently analyzed using liquid chromatography with ultraviolet detection (LC-UV). Some experimental parameters affecting the microextraction performance were studied and optimized. The proposed method was then applied to the analysis of various spiked soil samples and satisfactory analytical results were achieved.

## 2. EXPERIMENTAL

### a. Reagents and Samples

All reagents were of analytical grade. 1-Octanol and 1-decanol were purchased from Merck (Darmstadt, Germany). Propachlor, prometryn, HPLC grade acetonitrile (ACN), tetrahydrofuran (THF) and 1-undecanol were purchased from Sigma-Aldrich (Steinheim, Germany). Water was used after purification with a Milli-Q system (Millipore, Bedford, MA, USA).

Stock standard solutions were prepared in acetonitrile at a concentration of 100 µg/mL and stored at 4°C. The working solutions at different concentrations were freshly prepared by dilution of the stocks in mobile phase. Soil samples were taken randomly from five different places in the Zonguldak province, Turkey. After air-drying at room temperature, the samples were cleaned from all foreign materials, homogenized by blending in a porcelain mortar, and stored at 4°C in the glass bottles prior to analysis. In the optimization and validation assays, soil samples were spiked with standard solutions to reach required concentrations. Spiked samples were kept at room temperature for 60 min before being extracted.

### b. Instrumentation and Chromatographic Conditions

The liquid chromatographic system (Thermo Finnigan, San Jose, USA) consisted of a P1000 pump, a AS3000 automatic injector system, and a UV1000 UV detector. A Phenomenex $C_{12}$ Max-RP column (250×4.6 mm i.d., 4.0 µm) was used for separations. The mobile phase was a mixture of acetonitrile and % 0.1 aqueous acetic acid (50:50, v/v). The elution was performed in isocratic mode at a flow rate of 1.0 mL/min. The UV monitoring wavelength for quantification was set to 240 nm. A magnetic stirrer (Ika C-MAG HS 7), a centrifuge (Thermo Scientific Espresso Personal), and a multi plate shaker (Biosan MPS-1) were used for sample preparation.

### c. Supramolecular Solvent Production

For the preparation of the SUPRAS, 2.5 mL of 1-decanol was dissolved in 15 mL of THF and then 32.5 mL of distilled water was added to this solution. Immediately, a cloudy solution appeared along with the spontaneous formation of the SUPRAS in the bulk solution. The mixture was stirred with a magnetic stirrer (800 rpm) for 5 minutes. Then, the mixture was kept at room temperature for 5 minutes for the phase separation. The upper SUPRAS phase was collected by means of a microsyringe and stored in a refrigerator in a capped tube until use.

### d. Supramolecular Solvent-Based Microextraction Procedure

Homogenized soil sample (300 mg) was placed into the Eppendorf tube and 300 µL of SUPRAS was added. Afterwards, the mixture was vortex-mixed at 2500 rpm for 8 min and then centrifuged at 5000 rpm for 5 min. Finally, the supramolecular extract was collected with a microsyringe and transferred to a glass vial for the LC-UV analysis.

## 3. RESULTS AND DISCUSSION

Optimization of SUPRAS-based microextraction was carried out using soil subsamples (300 mg), spiked with propachlor and prometryn herbicides at a concentration of 1 µg/g each. The type of alkanol, composition and volume of SUPRAS, and vortex mixing time were the variables investigated. The optimal conditions were selected based on the extraction recoveries (ERs) of the herbicides. The ER was calculated as the ratio of the amount of the analyte in the collected SUPRAS phase to its initial amount in the sample. All the experiments were carried out in triplicate.

### a. Selection of SUPRAS-based Microextraction Conditions

It is important to select a suitable alkanol, because alkanol-based SUPRASs provide different types of interactions for medium polar and nonpolar analytes, namely hydrogen bonding in the polar groups and hydrophobic interactions in the hydrocarbons chains [9]. The short-chain alkanols

are better proton donors than longer ones, hence more capable of hydrogen bonding. While in the case of long-chain alkanols hydrophobic interactions become much stronger [13]. Three alkanols ($C_8$, $C_{10}$, and $C_{11}$) were used for the synthesis of SUPRASs and their extraction performances for the target herbicides were investigated. The experiments were carried out by using SUPRASs synthesized from 5% (v/v) alkanols and 30% (v/v) THF according to the procedure specified in Section 2.3. The extraction efficiencies using SUPRASs are shown in Figure 1. The results showed that extraction efficiency increased with the increasing chain length of alkanols. It seems that hydrophobic interactions between the herbicides and SUPRASs were the most contributing forces during extraction. The SUPRASs synthesized with 1-decanol and 1-undecanol were found to provide similar extraction efficiencies. However, 1-decanol was selected in SUPRAS formation process for the subsequent experiments based on its relatively low cost.
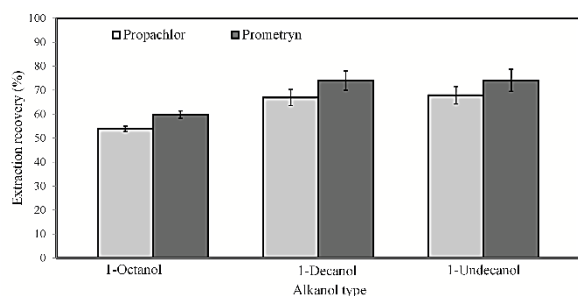


**Figure 1.** Effect of alkanol type. SUPRAS synthesis conditions; 5% (v/v) alkanol, 30% (v/v) THF and %65 (v/v) water. Microextraction conditions; 300 mg of soil, 500 μL of SUPRAS, 5 min of vortex mixing, spike level, 1 μg/g.

The SUPRASs are formed in a triple mixture of alkanol /THF/water, and the THF content of the mixture affects the composition and structure of SUPRASs [13]. For this reason, the percentage of THF used in the synthesis of SUPRASs is an important parameter that should be optimized. SUPRASs were synthesized using a constant concentration of 1-decanol (5%, v/v) and varying percentages of THF (10–50%, v/v) and a volume of 500 μL SUPRAS was used to extract the target herbicides from spiked soil samples. As can be seen in Figure 2, the extraction efficiency

increased with the increase of THF percentage up to 30% and remained nearly constant above this percentage. So, the optimal THF percentage was selected as 30% during the synthesis of SUPRAS.
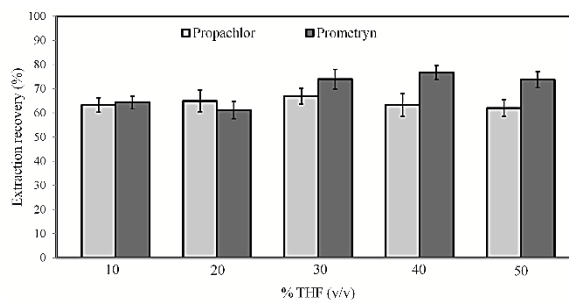


**Figure 2.** Effect of THF percentage. SUPRAS synthesis conditions; 5% (v/v) decanol, varying percentages of THF and water. Microextraction conditions; 300 mg of soil, 500 μL of SUPRAS, 5 min of vortex mixing, spike level, 1 μg/g.

Selection of the optimum volume for the extraction solvent is another important step in the majority of microextraction methods. By the increase of extraction solvent volume, the final solvent volume collected after centrifugation is increased, resulting in a decrease in sensitivity of the analytes. In order to increase sensitivity, it is essential to keep the volume of extraction solvent as low as possible. However, it is not always possible to reduce the solvent volume as desired, because an enough volume of solvent need to be collected after centrifugation for the analysis. To examine the effect of the extraction solvent volume on the extraction efficiency, different volumes of SUPRAS from 200 to 600 μL at 100-μL intervals were investigated. The obtained results (Figure 3) showed that the extraction efficiency was high in the SUPRAS volumes of 200 and 300 μL and decreased thereafter. Therefore, considering the high repeatability, 300 μL was selected as optimum SUPRAS volume.
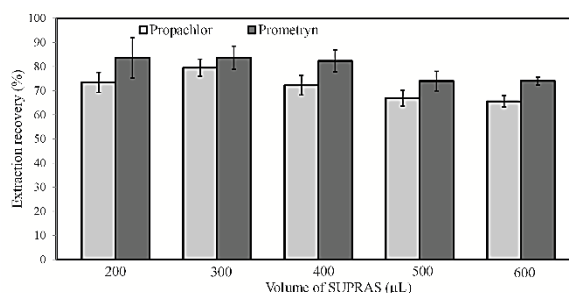


**Figure 3.** Effect of SUPRAS volume. SUPRAS synthesis conditions; 5% (v/v) decanol, 30% (v/v) THF and %65 (v/v)

water. Microextraction conditions; 300 mg of soil, varying volumes of SUPRAS, 5 min of vortex mixing, spike level, 1 µg/g.

The role of vortex mixing was to penetrate the extraction solvent into the soil particles more efficiently for the mass transfer of analytes to the extraction solvent. Therefore, the effect of vortex mixing time was examined within a range of 0–15 min at a constant speed setting of 2500 rpm. The experimental results are presented in Figure 4. The extraction efficiency was low when the extraction tube was vigorously shaken by hand for a few seconds (0 min). In the mixing process with vortex, there was a significant increase in the extraction efficiency by increasing the mixing time from 1 to 8 min. Above 8 min, no significant change in extraction efficiency occurred. The results showed that mass transfer of the herbicides to the SUPRAS phase reached equilibrium in 8 min. For this reason, 8 min was selected as the as the optimal vortex time.
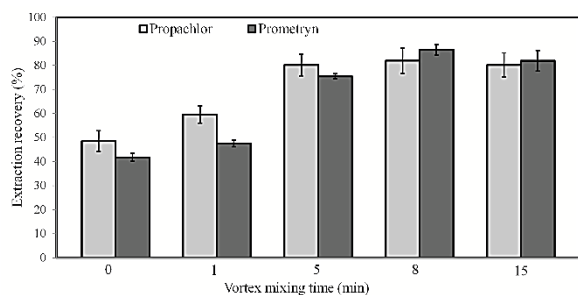


**Figure 4.** Effect of vortex mixing time. SUPRAS synthesis conditions; 5% (v/v) decanol, 30% (v/v) THF and %65 (v/v) water. Microextraction conditions; 300 mg of soil, 300 µL of SUPRAS, varying vortex mixing times, spike level, 1 µg/g.



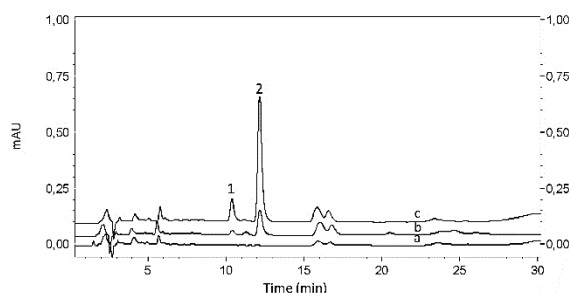**Figure 5.** LC–UV chromatograms of (a) a non-spiked soil sample, and the same sample after spiking of the herbicides at the (b) 1.0 and (c) 5 µg/g levels. 1: propachlor, 2: prometryn.

## b.   Analytical Performance of the Proposed Method

Analytical performance characteristics of the proposed method were obtained under the optimized conditions and shown in Table 1. Good linearity was obtained ranging from 0.25 to 20 µg/g for propachlor and 0.05 to 20 µg/g for prometryn with regression coefficients ($r^2$) higher than 0.9958. The limits of detection (LODs), based on a signal-to-noise ratio (S/N) of 3, varied between 0.01 µg/g (prometryn) and 0.07 µg/g (propachlor). The precision of the method was investigated with spiked concentration of 1 µg/g for five replicates in the same day and in five consecutive days. The relative standard deviations (RSDs) were lower than 8.8% (intra-day) and 12.1% (inter-day) for studied compounds. The mean extraction recoveries were 81% for propachlor and 87% for prometryn.

**Table 1.** Analytical performance of the SUPRAS-based microextraction method for the determination of herbicides in soil samples.

| Analyte | LR[a] | r[2b] | LOD[c] | LOQ[d] | RSD%[e] | RSD%[f] | ER% ± SD[g] |
|---|---|---|---|---|---|---|---|
| Propachlor | 0.25–20 | 0.9958 | 0.07 | 0.23 | 8.8 | 12.1 | 81 ± 5 |
| Prometryn | 0.05–20 | 0.9972 | 0.01 | 0.04 | 5.6 | 8.6 | 87 ± 3 |

[a]Linear range (µg/g).
[b]Square of correlation coefficient.
[c]Limit of detection  (µg/g, S/N = 3).
[d]Limit of quantification (µg/g, S/N = 10).
[e]Intra-day relative standard deviation (C = 1 µg/g, n = 5).
[f]Inter-day relative standard deviation (C = 1 µg/g, n = 5).
[g]Mean extraction recovery ± standard deviation (n = 3).

## c.   Sample Analysis

Soil samples collected from five different sampling points in Zonguldak, Turkey were analyzed with the proposed method for possible presence of the studied herbicides and none of them was detected in these samples. To test the accuracy of the proposed method, all the real samples were spiked at two concentration levels of 1 and 5 µg/g, and recoveries were calculated based on the amounts added and found. For each sample, the extraction was repeated three times. Relative recoveries and RSDs were calculated and listed in Table 2. The recoveries of herbicides in soil samples were all within the range 80-108%, with RSDs ranging from 2.1 to 8.1%. Fig. 5 shows, as an example, the LC–UV chromatograms of the herbicides extracted from a soil sample before and after spiking.

**Table 2.** Spiked recoveries of herbicides in soil samples.

| Samples | Added (µg/g) | Propachlor Found ± SD (µg/g) | RR% | RSD% | Prometryn Found ± SD (µg/g) | RR% | RSD% |
|---------|--------------|------------------------------|-----|------|-----------------------------|-----|------|
| Soil 1 | 1.0 | 0.84 ± 0.08 | 84 | 7.7 | 0.95 ± 0.06 | 95 | 5.8 |
|        | 5.0 | 4.48 ± 0.23 | 90 | 5.2 | 4.61 ± 0.12 | 92 | 2.6 |
| Soil 2 | 1.0 | 1.07 ± 0.07 | 107 | 6.8 | 0.91 ± 0.06 | 91 | 6.3 |
|        | 5.0 | 5.04 ± 0.21 | 101 | 4.1 | 4.67 ± 0.10 | 93 | 2.1 |
| Soil 3 | 1.0 | 0.94 ± 0.07 | 94 | 7.9 | 0.88 ± 0.04 | 88 | 5.1 |
|        | 5.0 | 5.38 ± 0.21 | 108 | 3.9 | 5.10 ± 0.13 | 102 | 2.5 |
| Soil 4 | 1.0 | 0.93 ± 0.08 | 93 | 8.1 | 0.92 ± 0.07 | 92 | 7.3 |
|        | 5.0 | 5.37 ± 0.23 | 107 | 4.3 | 5.05 ± 0.18 | 101 | 3.6 |
| Soil 5 | 1.0 | 0.80 ± 0.04 | 80 | 4.5 | 0.83 ± 0.05 | 83 | 5.5 |
|        | 5.0 | 4.34 ± 0.21 | 87 | 4.8 | 4.29 ± 0.34 | 86 | 8.0 |

RR: Relative recovery.
SD: Standard deviation (n = 3).

The SUPRAS-based microextraction method for the determination of herbicides in soil samples was compared with the existing methods in the literature [16–22]. The comparison details of the methods are given in Table 3. The proposed method offers a significant advantage in terms of the amount of sample and the volume of solvent used. The other applications require 0.5 g to 10 g of sample and 3 to 100 mL of solvent, while in the proposed method 0.3 g of soil sample and 0.3 mL of solvent are used. This makes the proposed method more economical. Moreover, the extraction time (8 min) of the proposed method is rather short compared to the extraction times (14 - 90 min) of some other methods. With respect to the extraction solvents, SUPRAS used in the proposed method is more environmentally friendly than organic solvents (acetone, dichloromethane, ethyl acetate, hexane, and acetonitrile) used in other methods. Some of the existing methods can be said to be better in terms of sensitivity due to their lower LOD values. In these methods, the use of higher amounts of sample and more precise detectors have provided better sensitivity. However, the methods using the UV detector have generally close LOD values. Regarding the precision and accuracy, the RSD and recovery values obtained in all methods present close similarity. From the comparison results, it should be concluded that the proposed SUPRAS-based microextraction method is a rapid, economical and environmentally friendly method for the determination of herbicides in soil samples

**Table 3.** Comparison of the proposed method with other methods used in determination of herbicides.

| Method | Analytes | Sample matrix | Sample amount (g) | Extraction solvent | Solvent volume (mL) | Extraction time (min) | RSD (%) | LOD (µg/g) | Recovery (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| MIP-SPE-LC-UV[a] | Propachlor | Soil and rice | 10 | Acetone + water | 60 | 90 | < 6 | - | 83 – 97 | [16] |
| ASE-GC-TSD[b] | Propachlor | Soil | 1 | Dichloromethane + acetone | 100 | 14 | < 8 | 0.005 | 82 – 115 | [17] |
| UE-GC-NPD[c] | Propachlor Prometryn | Soil | 5 | Ethyl acetate | 8 | 30 | - | 0.007 0.003 | 94 – 103 | [18] |
| MSPD-SPE-LC-DAD[d] | Prometryn | Seaweeds | 1 | Ethyl acetate + hexane | 25 | - | < 7 | 0.0014 | 83 – 97 | [19] |
| MIP-DSPE-LC-UV[e] | Prometryn | Grape seeds | 0.5 | Acetonitrile | 3 | 30 | < 10 | 0.013 | 81 – 95 | [20] |
| MSPD-LC-DAD[f] | Prometryn | Mussel | 0.5 | Ethyl acetate + acetonitrile | 25 | - | < 16 | 0.049 | 84 – 94 | [21] |
| CPE-LC-UV[g] | Prometryn | Soil | 2 | Triton X-114 + water | 10 | 30 | < 2 | 0.004 | 85 – 94 | [22] |
| SUPRAS-ME-LC-UV[h] | Propachlor Prometryn | Soil | 0.3 | SUPRAS | 0.3 | 8 | < 12 | 0.07 0.01 | 80 - 108 | This work |

[a]MIP-SPE-LC-UV: Molecularly imprinted polymer-solid phase extraction-liquid chromatography-ultraviolet detector
[b]ASE-GC-TSD: Accelerated solvent extraction-gas chromatograph-thermionic specific detector
[c]UE-GC-NPD: Ultrasonic extraction- gas chromatograph-nitrogen–phosphorus detector
[d]MSPD-SPE-LC-DAD: Matrix solid phase dispersion-solid phase extraction-liquid chromatography-diode array detection
[e]MIP-DSPE-LC-UV: Molecularly imprinted polymer-dispersive solid-phase extraction-liquid chromatography-ultraviolet detector
[f]MSPD-LC-DAD: Matrix solid-phase dispersion-liquid chromatography-diode array detection
[g]CPE-LC-UV: Cloud-point extraction-liquid chromatography-ultraviolet detector
[h]SUPRAS-ME-LC-UV: Supramolecular solvent-based microextraction-liquid chromatography-ultraviolet detector

## 4. CONCLUSIONS

Today, it is known that herbicides with many different chemical structure and mode of action are used to increase the yield of agricultural products. Therefore, it is important to monitor the herbicides in the environment and food sources in order to protect the environment and human health. In this work, an analytical method has been optimized and validated for the determination of selected herbicides in soil samples. For this purpose, propachlor (amide group) and prometryn (triazine group) having different functional groups were chosen as model herbicides. The results obtained in the analysis of soil samples confirmed that SUPRAS-based microextraction method can be successfully applied in the determination of the selected herbicides. It is also expected to be applied in the analysis of multiclass herbicides in the field of food analysis with some modifications.

## Acknowledgements

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