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Screening Design of Experiment Applied to Dispersive Liquid-Liquid Microextraction of UV Filters from Water

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Abstract: A Plackett-Burman factorial design (PBD) has been used for the optimization of dispersive liquid-liquid microextraction (DLLME) of UV filters from water. The experimental procedure included a DLLME sample preparation prior to high-performance liquid chromatography triple quadrupole mass spectrometry (HPLC-MS/MS) measurements. The variables of the DLLME process for simultaneous preconcentration of UV filters (avobenzone and octocrylene) have been studied using PBD with twelve experimental runs. Several experimental variables including the extractant type, pH value, the disperser type, extractant volume, disperser volume, vortexing/sonication, centrifugation speed, reconstitution solvent, salt content, temperature, and centrifugation time were considered in the optimization process. PBD results revealed the most important variables that affected the extraction efficiency (EF). The first three most influential variables, as showed using a Pareto graph, were in the following order: the extractant volume > the disperser type > the extraction temperature. Based on the main effects plot, it was revealed that some variables (pH value, the disperser type, extractant volume, temperature, centrifugation speed, salt content) increased over the experimental domain, while the others (the extractant type, disperser volume, vortexing/sonication, centrifugation time, reconstitution solvent) decreased.

Keywords: UV filters, Plackett- Burman, DLLME, HPLC-MS/MS

Introduction

Organic UV filters are the main ingredients in many personal care products intended to protect users from UV solar radiation (Chisvert & Salvador, 2018). The daily use of these products has led to the increased detection of UV filters in water samples. The wide range of UV filters discovered in water samples around the World has caused concern due to the persistence of these compounds, as well as the harmful biological effects on aquatic organisms (Brausch & Rand, 2011). Since the complexity of the matrix and low concentrations of UV filters in the environmental water samples, a pre-treatment step for sample enrichment and clean-up is necessary.

Recently, in addition to traditional techniques, alternative ones such as dispersive liquid-liquid microextraction (DLLME) have been used for this purpose (Ramos et al., 2019). This technique is based on a ternary solvent system comprising an aqueous donor sample, an organic extraction solvent (non-miscible in water), and a disperser solvent (miscible in both extraction and donor phases) (Chisvert, Benedé, & Salvador, 2018).

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A large number of the DLLME experimental variables should be studied in order to optimize the analytical recovery. Traditional the one-variable-at-a-time (OVAT) optimization approach, in which one variable is changed while keeping all others constant, is time-consuming and inefficient to study the interactions among the variables. The modern approach to the optimization uses the design of experiment (DOE) methodology that enables all variables to be changed at the same time (Onjia, 2016). Plackett-Burman DOE (PBD), as one of the most frequently used variables screening tool, is applied in this work to optimize DLLME of octocrylene and avobenzone from water.

Method

The variables of the DLLME process for simultaneous preconcentration of octocrylene and avobenzone have been studied using PBD with twelve experimental runs. Several experimental variables including volume (V_{ex}, V_{disp}) and type (Ex, Disp) of both dispersive and extraction solvents, pH value, vortexing/sonication (Vor/US), temperature (T_{ex}), centrifugation speed (r_{centr}), reconstitution solvent (R_{st}), the salt content (NaCl) and centrifugation time (t_{centr}) were considered in the optimization process.

Table 1. The variables included in the PBD and their values

Run	pH	Ex	Disp	V_{ex}	V_{disp}	Stir	T_{ex}	t_{centr}	r_{centr}	R_{st}	NaCl
1	8	$CHCl_3$	MeOH	400	600	Vor	25	2	2000	MeOH	10
2	2	C_2Cl_4	MeOH	200	1000	Vor	5	2	2000	MeOH	0
3	2	$CHCl_3$	MeOH	200	1000	US	25	7	2000	ACN	10
4	8	C_2Cl_4	ACN	200	1000	Vor	25	7	4000	MeOH	10
5	2	C_2Cl_4	ACN	400	1000	Vor	25	7	2000	ACN	0
6	8	$CHCl_3$	MeOH	400	600	Vor	5	7	4000	ACN	0
7	8	C_2Cl_4	MeOH	200	1000	US	25	2	4000	ACN	0
8	8	C_2Cl_4	ACN	400	600	US	5	2	2000	ACN	10
9	2	C_2Cl_4	MeOH	400	1000	US	5	7	4000	MeOH	10
10	2	$CHCl_3$	ACN	200	600	Vor	5	2	4000	ACN	10
11	8	$CHCl_3$	ACN	200	600	US	5	7	2000	MeOH	0
12	2	$CHCl_3$	ACN	400	600	US	25	2	4000	MeOH	0

Ten milliliters of water containing target analytes were pipetted into a 15 mL centrifuge tube. Next, different amounts of NaCl (0-10 %) were added. The pH effect on the OC and AVO extraction from the sample solution was studied within the range of 2-8 using HCl and NaOH. When the required sample temperature was reached, a mixture of extraction and disperser solvents was added. The sample solutions were shaken for 1 min using US irradiation or vortex agitator. After centrifugation, the organic phase was withdrawn through a syringe and evaporated under nitrogen steam. The residue was dissolved with 200 µL of reconstitution solvent. Finally, 10 µL of the solution was injected into the HPLC-MS/MS system for analysis.

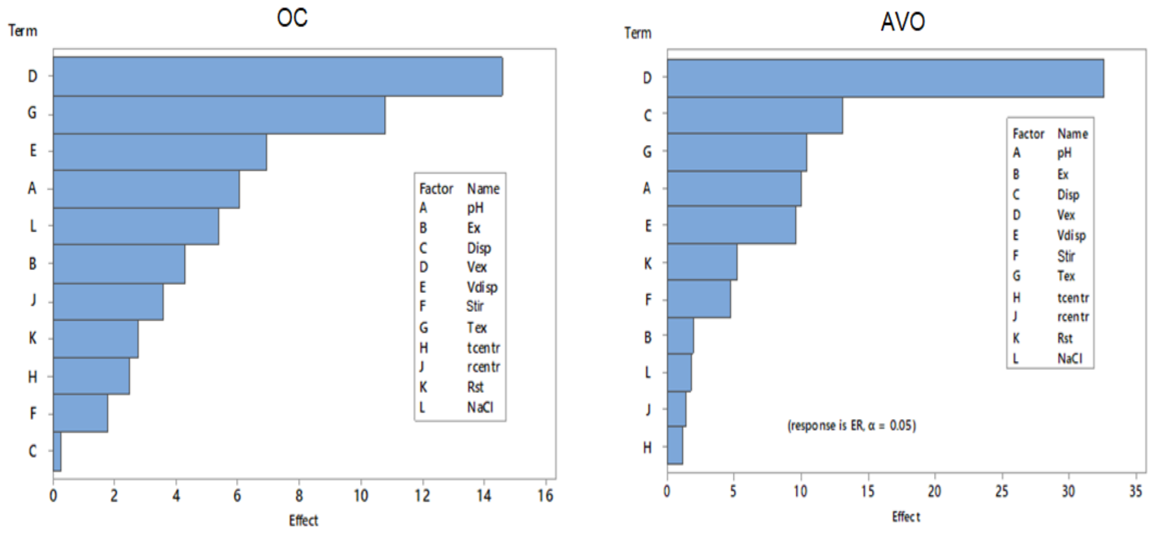

Figure 1. Pareto chart of investigated effects in the screening PBD.

Results and Discussion

Graphical data representations, Pareto chart (Fig. 1), and main effect graphs (Fig. 2) can be used to find the relationship between input variables and system responses. The effect of a variable is the change in response that is caused by a change in the level of the variable. The Pareto chart represents the ANOVA effect estimates that are sorted from the largest absolute value to the smallest one.

Results indicate that the volume of extraction solvent, temperature, the volume of disperser solvent, and pH of aqueous solution were the most significant variables and were estimated for further assessment in DLLME of avobenzone. C_2Cl_4, MeOH and ACN, are selected as the extraction, disperser, and reconstitution solvent, respectively. This selection significantly improved DLLME performances for both analytes.

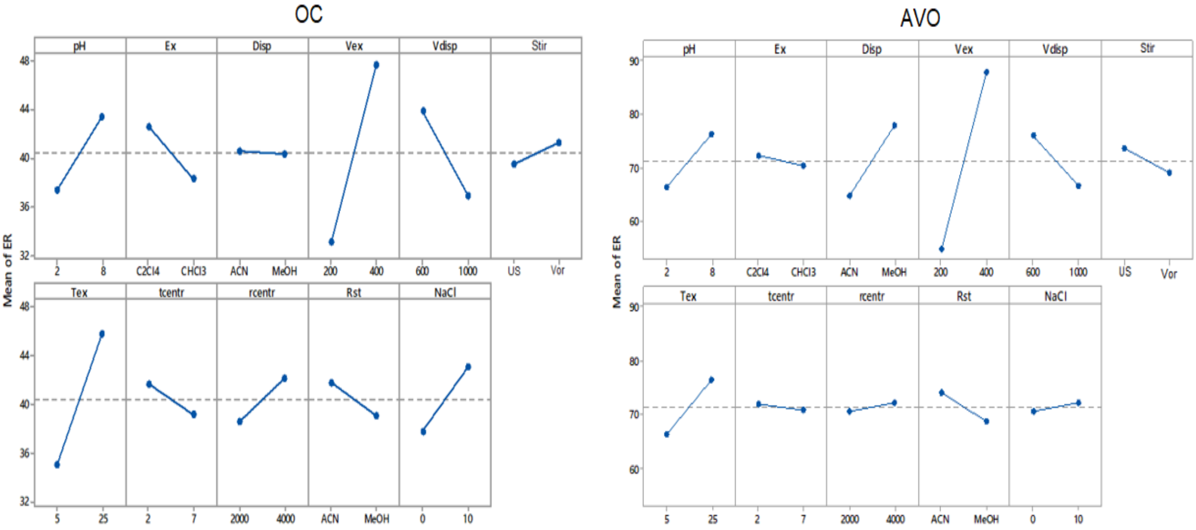

Figure 2. Main effects graph of variables in the screening PBD.

Fig. 2. shows the main effects graph of variables in the screening PBD. These results are used to analyze differences among level for variables. The response for each variable level connected by a line is plotted. The main effect plots reveal whether the responses differ at different levels. The slopes on two-level plots shown in Fig. 2 are the main effects. In the case of avobenzone, the least important variable is the type of dispersant. For DLLME of octocrylene, four variables: the type of extraction solvent, the salt content, centrifugation speed, and centrifugation time have the lines connecting the responses at both levels parallel to the x-axis with the slopes close to zero. It means that their influences on DLLME performances could be neglected.

Both the avobenzone and octocrylene extraction efficiencies are most dependents on the extractant solvent volume. Based on the liquid-liquid extraction theory, the analyte migration rate from aqueous into the organic phase is proportional to the organic-phase volume since the interfacial area between the two liquid phases is directly related to this volume. However, it should bear in mind that when the extractant solvent volume increases, i.e., the extractant/sample volume ratio increases, the enrichment factor decreases.

In this study, this volume was studied in the range of 200 - 400 µL. It was observed that at 400 µL, the extraction efficiencies for both analytes are at their maximum. Hence, 400 µL of C_2Cl_4 was chosen as the optimum extractant solvent volume. The enrichment factors of avobenzone and octocrylene were in the range of 40 - 50, and the sample preparation is very time-saving. These results indicated the successful application of the DLLME technique in the preconcentration of low concentration UV filters, such as avobenzone and octocrylene, in water samples.

Conclusion

DLLME technique represents an improvement in the sample preparation, which especially addresses the issues of miniaturization and time efficiency. PBD has generated the most information about the DLLME process for the fewest optimization runs. It identified the most influencing DLLME variables. Also, the main effects in the system have been estimated. A large number of variables analyzed simultaneously are reduced to a few to be examined more closely. The most critical variable in this work is the extractant volume, both for avobenzone and octocrylene DLLME.

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