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Optimization of a UV-Visible Spectrophotometer Response Using a Fractional Factorial Design

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Abstract

Three operation parameters of a UV-visible spectrophotometer (scan speed, monochromator slit width, and sampling interval) were optimized utilizing a fractional factorial design. Four absorption spectra of holmium oxide were recorded in a portion of the visible region (560-610 nanometers) using different combinations of "high" and "low" levels for the parameters already mentioned. The combinations were provided by a 2^{3-1} design. From the results it is deduced that the highest quality spectrum is furnished by the following combination: high scan speed, narrow monochromator slit width (0.2 nm.) and small sampling interval (one data point per each 0.1 nanometer). This work illustrates the usefulness of fractional factorial design as an optimization tool in the analytical chemistry laboratory.

Keywords. UV-visible spectroscopy, fractional factorial design, optimization.

Resumen

Tres parámetros de operación de un espectrofotómetro UV-visible (velocidad de barrido, ancho de ranura del monocromador e intervalo de muestreo) fueron optimizados utilizando un diseño factorial fraccionado. Cuatro espectros de absorción de óxido de holmio fueron registrados en una porción de la región visible (560-610 nanómetros) usando diferentes combinaciones de niveles "altos"y "bajos" para los parámetros ya mencionados. Las combinaciones fueron provistas por un diseño 2^{3-1}. De los resultados se deduce que el espectro de más alta calidad es proporcionado por la siguiente combinación: alta velocidad de barrido, ancho de ranura del monocromador pequeño (0.2 nanómetros) e intervalo de muestreo pequeño (un punto por cada 0.1 nanómetro). Este trabajo ilustra la utilidad del diseño factorial fraccionado como una herramienta de optimización en el laboratorio de química analítica

Palabras Clave. Espectroscopía UV-visible, diseño factorial fraccionado, optimización

Introduction

UV/visible absorption spectroscopy is one of the most widely utilized techniques for quantitative and qualitative chemical analysis. This type of spectroscopy employs a spectrophotometer which records the different frequencies of UV/visible radiation absorbed by a species and translates these measurements into a graphic output known as absorption spectrum. Typically, a spectrophotometer has five basic components namely, a radiation source, a sample holder, a frequency selector or monochromator, a detector, and a read-out device.

The absorption spectrum quality critically depends on some operation parameters which can be tuned by the experimenter [1]. For example, monochromator slit width can be reduced to improve spectrum resolution. A narrow slit width produces sharper, more defined peaks, however there is a limit beyond which further slit width reduction causes a significant decrease of radiant signal power making it difficult to measure. Hence, it is advisable to reduce the slit width only enough to obtain a spectrum with good resolution. The scan speed also affects spectrum quality. Slow scan speeds produce spectra with good level of detail; on the other hand, high scan speeds produce less detailed spectra. Sampling interval, that is, the number of points per wavelength unit

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recorded by the instrument is another parameter that influences spectrum quality. A small sampling interval leads to a detailed spectrum; the opposite is observed when a large sampling interval is used. Once the factors affecting the spectrum quality have been identified, the experimenter has to devise a set of experiments which will provide information about the combination of parameter settings that produce the optimal response. Because of its advantages, fractional factorial analysis is the most appropriate for such a purpose. In fact, fractional factorial analysis has proved to be a very useful tool for optimization of a variety of chemical systems [2, 3].

Methods

The optimal response of a process or analysis may be obtained from the proper combination of levels for the factors that influence such response. Experimental design methods provide strategies for systematically varying the values of these factors until the combination that guaranties the best result is found. They furnish the minimum number of experiments necessary for optimizing a system [4]. The experimental design methods most commonly used for optimizing chemical procedures are full factorial and fractional factorial designs.

In the simplest version of full factorial design, two levels known as "high" and "low" are attributed to each factor. The levels are selected by the experimenter based on his experience and knowledge of the process. The number of experiments to be performed is given by $2n$, with n being the amount of factors under study. This number provides all the possible combinations of levels for the factors. The low level is usually represented by a minus sign and the high level by a plus sign. For instance, a full factorial design for three factors (A, B and C) consists of the following eight experiments:

Experiment Number	A	B	C	Response
1	-	-	-	y_1
2	+	-	-	y_2
3	-	+	-	y_3
4	+	+	-	y_4
5	-	-	+	y_5
6	+	-	+	y_6
7	-	+	+	y_7
8	+	+	+	y_8

Table 1: A full factorial design with three factors.

This arrangement is called *experimental matrix* and it is constructed as follows: in the first column, one "-" and one "+" signs are alternated until the 2^n entries are completed. In the second column, two "-" and two "+" signs are alternated; and in the third, four "-" and four "+" signs are alternated [5]. In general, for column j, 2^{j-1} "-" signs and 2^{j-1} "+" signs are alternated. Such procedure guaranties each experiment is a unique combination of levels. From the experimental matrix the following items can be calculated:

- The average response
- The main effects (effects of the original factors)
- The effects of multiple-factor interactions (synergy or antagonism effects among two, three or more factors)
- The effect of the interaction among all the factors under consideration.

In some occasions, the number of factors under study may be large and consequently the amount of experiments to perform in a full factorial design becomes too high. For instance, 6 factors require 64 experiments, which are already a lot either in the laboratory or at industrial level, 7 factors require 128 experiments, 8 factors require 256 experiments and so on. Full factorial designs require so many experiments because they evaluate the importance of not only the main effects but also the multiple-factor interactions [6]. In practical applications it is fairly uncommon that interaction effects of more than two factors affect the response. In fact, $n+1$ experiments is the minimum requirement to evaluate the effect of n factors.

Fractional factorial designs take advantage of the generally correct assumption that interaction effects of order higher than two are negligible to drastically reduce the number of experiments to be carried out. In these designs the required number of experiments is given by 2^{n-p} where n is the number of factors and p is the "degree of fractioning" which can assume the values $1, 2, ..., n-1$. The experimental matrix for a 2^{3-1} fractional factorial design is as follows:

Experiment Number	A	B	C	Response
1	-	-	+	y_1
2	+	-	-	y_2
3	-	+	-	y_3
4	+	+	+	y_4

Table 2: A 2^{3-1} fractional factorial design.

For the first two factors (A and B) the signs "-" and "+" are alternated in identical way of a complete design, but for third factor (C) a sequence of signs corresponding to the interaction of the first two is used. It is inevitable to lose some information, but instead of eight experiments now only four are required to optimize the response.

Factor	**-**	**+**
Scan speed (X_1)	Low	High
Slit width (X_2)	0.2 nm	5 nm
Sampling interval (X_3)	0.1 nm	2 nm

Table 3: Levels for the factors under study

Experiment Number	X_1	X_2	X_3
1	-	-	+
2	+	-	-
3	-	+	-
4	+	+	+

Table 4: Experimental design used in this work

Results y Discussion

Holmium oxide was used as analite. This compound features an important number of sharp, stable absorption peaks in the region between 240 and 640 nanometers. Because of such characteristics, holmium oxide is a standard to validate the wavelength scale of a UV/visible spectrophotometer [7]. A 2^{3-1} fractional factorial design was applied using scan speed, monochromator slit width, and sampling interval as factors. Factor levels are included in Table 3.

The experimental matrix for the proposed design is presented in Table 4. The experiments were carried out in a Shimadzu 1201S UV/visible spectrophotometer. This is a programmable, single beam instrument which works in the spectral region between 220 and 1100 nanometers.
Figure 1 shows the spectra obtained from the four experiments generated by the design. Each spectrum was graded according to its quality in a scale from 0 to 100 and those values were utilized as the responses for the analysis. Table 5 presents such results.

Experiment Number	X_1	X_2	X_3	**Response**
1	-	-	+	75
2	+	-	-	95
3	-	+	-	90
4	+	+	+	70

Table 5: Experimental matrix including responses

Yates algorithm [8] was used to estimate the factor effects. The following values were obtained,

Average response:	82.5
X_1 effect:	0.0
X_2 effect:	-5.0
X_3 effect:	-20.0

Table 6: Main factor effects.

Because for this design interaction effects cannot be distinguished from main effects, the interpretation of the results is centered exclusively in the main factor effects. It is observed that the effect of changing the scan speed level from low to high while keeping constant the other factors does not alter the response. On the other hand,

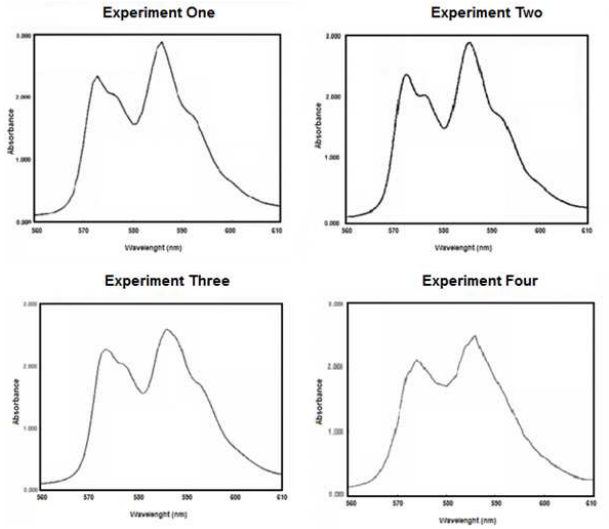

Figure 1: Spectra obtained performing the experiments generated by the fractional factorial design. The region between 560 and 610 nanometers was scanned.

the effect of changing the slit width level from low to high while keeping constant the other factors produce a 5 unit decrease in the response. Finally, the effect of changing the sampling interval level from low to high while keeping constant the other factors produces a 20 unit decrease in the response. These results suggest that in order to obtain the best response, the monochromator slit width and sampling interval should be kept at low levels to avoid a decrease in the response, while scan speed could assume either of its two levels because it has no effect on the response. From the available experiments, the only one that meets the conditions stated above is experiment number two (+, -, -). Therefore, this one was selected as the most appropriate combination of factor levels to obtain the best instrumental response.

Conclusions

A fractional factorial experimental design was applied to optimize the response of a UV/visible spectrophotometer. Three instrument operation parameters (scan speed, monochromator slit width, and sampling interval) were considered and a 2^{3-1} design was utilized. The combination of high scan speed, narrow monochromator slit width, and low sampling interval produces the optimal response. The work illustrates the usefulness of this type of experimental design for optimization purposes in the analytical chemistry laboratory.

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