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Multivariate technique for optimization of digestion procedure by focussed microwave system for determination of Mn, Zn and Fe in food samples using FAAS

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Abstract

This article describes the development by response surface methodology (RSM) of a procedure for iron, zinc and manganese determination by flame atomic absorption spectrometry (FAAS) in food samples after digestion employing a focussed microwave system. A Doehlert matrix was used to find optimal conditions for the procedure through response surface study. Three variables (irradiation power and time and composition of oxidant solution—$HNO_3 + H_2O_2$) were regarded as factors in the optimization study. The working conditions were established as a compromise between optimum values found for each analyte taking into consideration the robustness of the procedure. These values were 12 min, 260 W and 42% (v/v) for irradiation time, irradiation power and percent of H_2O_2 in solution, respectively. The accuracy of the optimized procedure was evaluated by analysis of certified reference materials and by comparison with a well-established closed vessel microwave dissolution methodology.

Keywords: Multivariate optimization; Doehlert matrix; Iron; Zinc; Manganese; FAAS

1. Introduction

It is well known that microwave electromagnetic radiation has not energy enough to break chemical bonds, just affecting the orientation of ions and molecules according to the electromagnetic field intensity, promoting a fast increase of the temperature of the absorbent media through ionic conduction and dipole rotation primary mechanisms [1]. Basically, microwave technology can be divided in systems with opened and closed flasks. The use of microwave ovens with closed flasks (diffuse microwaves) in sample preparation decrease or even eliminate losses of volatile elements, reduces analytical blank values and keeps the acid mixture isolated during whole process, which really diminishes sample contamination. However, these systems present some limitations in terms of the amount of sample that can be treated and eventually present safety problems because of the high pressures developed inside the flasks. On the other hand, in microwave ovens with opened flasks, also called focussed microwave ovens, highest masses of sample can be digested without risk of excessive increase of the inner pressure of the system because the gases generated during digestion are continuously removed, allowing furnace operation at atmospheric pressure and temperatures near to the boiling point of acid mixture [2]. Other advantage observed in the use of focussed systems is the lower time required to heat the solutions since the microwaves are not dispersed over the

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cavity of the oven, being concentrated on the small portion of sample [3].

One of the most common applications of the microwave digestion is for the determination of total metal contents in organic samples by destruction of carbon metal bonds. Following this concept, several digestion procedures using microwave energy has been developed for this purpose. Smith and Arsenault have published an extensive review about this theme [4].

The present paper describes the development, by response surface methodology (RSM), using a Doehlert matrix for three variables (irradiation time and power and composition of the oxidant mixture) of a procedure for iron, zinc and manganese determination by flame atomic absorption spectrometry (FAAS) in food samples after their optimised digestion in a focussed microwave digestion system.

1.1. Analytical procedures for optimization by Doehlert design

The optimization of analytical methods can be performed by two different ways: conventional univariate methodology, typically represented by a process where “one variable is studied at each time”, which has an easier interpretation but requires greater amounts of reagent and time to be accomplished. Besides, interactions among variables are not considered. The other way entails multivariate techniques, which are faster, more economical and effective, and allow more than one variable to be optimised simultaneously. The RSM is a multivariate technique, which fits mathematically the experimental domain studied in the theoretical design through a response function [5,6]. However, in order to determine the real function established among the analytical response and the significant factors, second order designs are used as Central composite, Box-Behnken or Doehlert matrix [7]. Central composite is the most used approach but Doehlert and Box-Behnken designs require lower number of experiments (N). For Doehlert and Box-Behnken designs, $N = k^2 + k + 1$, where k is the number of variables under study.

Another advantage of the Doehlert designs over the Central composite approach is its higher efficiency value (ϕ), which is determined by dividing the coefficient number of the quadratic equation (p) by the number of experiments (N) required for the design [8]. For Doehlert designs with $k = 3$, N is equal to 13 and p is 10 yielding a $\phi = 0.77$. In turn, for central composite designs with the same $k = 3$, N is 15, p is 10 and then $\phi = 0.67$.

Doehlert matrix was proposed as statistical experimental design in 1970 [9], but only now this design has been more used [10]. The first application in Analytical Chemistry was carried out for optimization of a separation process using HPLC [11]. Since then, several articles with two-variables Doehlert design have been issued, including procedures using solid phase spectrophotometry [12], simultaneous solvent extraction of several metals [13], and on-line system for preconcentration and determination of zinc by inductively coupled plasma optical emission spectrometry [14]. Optimization processes that involve simultaneously more than two variables have not been so widespread. Three-variables Doehlert designs were only used for interpretation of atomisation interferences in molybdenum determination using electrothermal atomic absorption spectroscopy [15], in a procedure for germanium determination by spectrofluorimetry [8,16], optimization of the experimental conditions for kynurenic acid determination by adsorptive stripping voltammetry [17], optimization of extraction process of arsenic species from mussels using microwaves [18], optimization of procedure using micellar electrokinetic capillary chromatography for separation of alkaloids [19] and glucosinates [20]. A four-variable Doehlert design was used for optimization of procedure for nimesulide determination by adsorptive stripping voltammetry [21]. Our research group have been used Doehlert matrix for optimization of preconcentration procedure for determination of molybdenum [22] in seawater samples by ICP OES, on-line preconcentration systems for copper [23] and lead [24] determination by flame atomic absorption spectrometry, and optimization of instrumental conditions in GFAAS [25–27].

2. Experimental

2.1. Instrumentation

A Perkin-Elmer 3100 flame atomic absorption spectrometer was used for the analysis. Manganese, zinc and iron hollow cathode lamps were run under operational conditions suggested by the manufacturer. These conditions are shown in Table 1. All measurements were performed with an air-acethylene flame with flow rates of 13.51 and 2.0l min^{-1}, respectively.

A focussed Prolabo microwave oven with only one cavity, model Soxwave 100 (Fontenay-sous-Bois, France) equipped with a quartz flask and a top condenser was used. Power settings from 60 to 300 W could be applied in steps of 10 W and the microwave energy was focussed into quartz vessel under atmospheric pressure.

A closed vessel microwave digester system model CDS 7000 from Spex (Metuchen, NJ, USA) was used to the digestion of a commercial food sample (wheat flour I) in order to use it as reference along the study. This system was also used in the dissolution of other commercial samples aiming the comparison of the two procedures.

Table 1
Operational conditions employed by FAAS determination

Parameter	Mn	Zn	Fe
Lamp current (mA)	5.0	5.0	4.0
Wavelength (nm)	279.5	213.9	248.3
Silt bandwidth (nm)	0.2	1.0	0.2
Burner height (mm)	13.5	13.5	13.5

2.2. Reagents and solutions

All reagents were of analytical grade unless otherwise stated. Ultra pure water was obtained from a Simplicity Milli-Q system (Millipore). Nitric acid and hydrogen peroxide were supplied by Merck (Darmstadt, Germany). All laboratory glassware was kept overnight in 10% (v/v) nitric acid solution. Before use, the glassware was rinsed with ultra pure water and dried in a dust free environment.

Manganese, iron and zinc solutions were prepared by diluting a 1000 $\mu g\,ml^{-1}$ standard solution (Merck) with a 1% (v/v) hydrochloric acid solution.

2.3. Closed vessel microwave oven digestion procedure

The methodology using a closed vessel microwave oven was used as reference since it was successfully applied by our research group [28] in the dissolution of several types of organic certified reference materials.

All samples (commercial and certified reference materials) were digested according to the following procedure: first, all samples were dried overnight at 110 ± 5 °C in an electrical oven. After cooling, 0.5 g of each sample was carefully weighed into the own PFA liners of the oven and 8 ml of concentrated nitric acid was added. After standing overnight in contact with nitric acid, 2 ml of 30% m/m hydrogen peroxide was added and the liners were closed, placed into the microwave oven cavity and two irradiation cycles of 25 min (1000 W maximum power) were run. The program of the equipment was adjusted to avoid internal pressures higher than 180 psig and temperatures higher than 190 °C and between the first and second cycle the liners were opened in order to release gases formed during digestion. Applying this procedure, perfectly clear and colourless solutions were obtained. Then, this solution was transferred to the volumetric flask and the volume was made up to 25 ml. This final solution was employed in the Fe, Mn and Zn determination by flame atomic absorption spectrometry.

3. Optimization strategy

For the optimization study using focussed microwave oven a commercial food sample (wheat flour I) was used throughout. This sample was analysed by FAAS after its closed vessel microwave digestion and its contents for manganese, iron and zinc determined. These values were used for achievement optimization. For the experiments 0.5 g of the food sample (wheat flour I) was placed in an open reflux microwave oven vessel. To this sample mass 10 ml of deionised water and 10 ml of a solution of HNO_3/H_2O_2 at certain proportion defined by the experimental design were added. Focussed microwaves were then applied at conditions also defined by the experimental design for each numbered experiment. After digestion, the irradiated sample was transferred to 25 ml volumetric flask and the volume was completed to the mark. The concentration of the analytes in this solution was analysed by FAAS using external calibration approach. The Mn, Zn and Fe concentrations were compared with those obtained when using the closed vessel microwave digestion for recovery studies.

The optimization process was carried out using response surface methodology. A Doehlert matrix was used for the optimization of three experimental variables: irradiation time (T), irradiation power (P) and hydrogen peroxide volumetric percentage in the solution HNO_3/H_2O_2 (%H_2O_2). In this case T was studied at seven levels, P at five levels and %H_2O_2 at three levels. The Doehlert design for these three variables is shown in Table 2. The experimental data were processed by using STATISTICA software [29] and duplicates at the central point were performed in order to estimate experimental variance.

In the case of three variables designs, a cuboctahedron is produced geometrically through a uniform distribution of points over the whole experimental region. A cuboctahedron is a geometrical solid with eight vertices symmetrically truncated producing eight equilateral triangles whose edges are equal to those of the remaining squares. Fig. 1

Table 2
Doehlert design for optimization of irradiation time, irradiation power and oxidant mixture composition

Number	Time (min)	Power (W)	HNO_3/H_2O_2 (% v/v H_2O_2)	Recovery (%)[a]		
				Fe	Zn	Mn
01	14 (0.866)	120 (−0.5)	30 (0)	74.80	74.06	80.59
02	14 (0.866)	240 (0.5)	30 (0)	99.49	97.81	98.03
03	12 (0.577)	180 (0)	50 (0.816)	65.56	76.89	93.78
04	10 (0.289)	120 (−0.5)	10 (−0.816)	76.29	77.17	94.30
05	10 (0.289)	240 (0.5)	10 (−0.816)	83.18	75.83	91.31
06	8 (0)	60 (−1)	30 (0)	62.82	68.08	89.45
07	8 (0)	180 (0)	30 (0)	100.65/108.0	100.03/101.45	99.00/100.30
08	8 (0)	300 (1)	30 (0)	100.87	99.76	98.46
09	6 (−0.289)	120 (−0.5)	50 (0.816)	75.82	93.36	94.87
10	6 (−0.289)	240 (0.5)	50 (0.816)	64.93	102.77	91.95
11	4 (−0.577)	180 (0)	10 (−0.816)	49.41	53.10	82.62
12	2 (−0.866)	120 (−0.5)	30 (0)	68.21	37.41	80.21
13	2 (−0.866)	240 (0.5)	30 (0)	74.71	37.32	77.84

[a] Based on the closed vessel microwave digestion and FAAS determination of Fe, Zn and Mn in the wheat flour I sample.

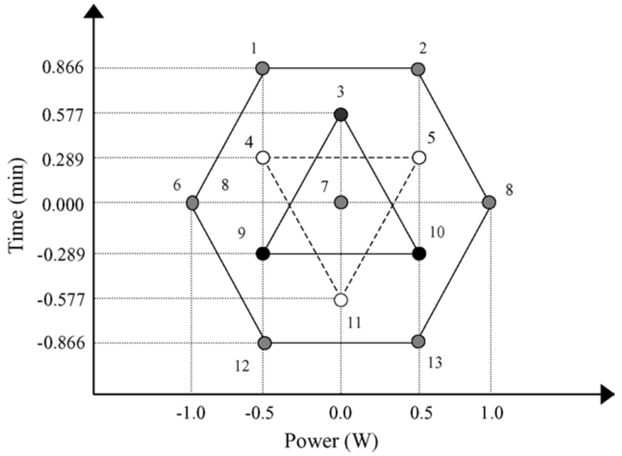

Fig. 1. A cuboctahedron plane projection used in this work for three variables optimization.

shows the plane projection of the cuboctahedron used in this work.

The theoretical Doehlert matrix leads to a theoretical experimental design set with real values can be deducted. Relation between coded values (C_i) and real values (X_i) is given by

$$C_i = \left(\frac{X_i - X_i^0}{\Delta X_i}\right)\alpha$$

where X_i^0 is the real value at the centre of the experimental domain, ΔX_i the step of variation of the real value, and α is equal to 1, 1 and 0.707 for the first, second and third factor, respectively.

3.1. Determination of the critical point

Considering an optimization design of a process which has three experimental variables (*A*, *B* and *C*) and the experimental response (*Y*), for a second order model, the experimental data can be fit as the following equation:

$$(Y) = a + b(A) + c(B) + d(C) + e(A)^2 + f(B)^2 + g(C)^2 + h(A)(B) + i(A)(C) + j(B)(C) \qquad (1)$$

where (*Y*) is the experimental response to be optimised; (*a*), the constant term; (*b*), (*c*) and (*d*) are coefficients of the linear terms; (*e*), (*f*) and (*g*) are coefficients of the quadratic terms and (*h*), (*i*) and (*j*) are coefficients of interaction between the three factors.

The Lagrange criterion is used to characterise the response function and establish the second derivatives of this function in order to evaluate the critical point (A_c, B_c, C_c). The quadratic equations only show one critical point, where four situations are then possible:

(1) There is not any information: $\Delta_2 = 0$.
(2) Relative maximum: $\Delta_1 < 0$; $\Delta_2 > 0$; $\Delta_3 < 0$.
(3) Relative minimum: $\Delta_1 > 0$; $\Delta_2 > 0$; $\Delta_3 > 0$.
(4) Saddle point: none of above situations is present.

Saddle point is defined as the critical point of a surface response, which presents maximum response for levels of some variables and simultaneously minimum response for levels of other variables of the analytical system studied.

The Hessian determinant (Δ_3) of the function *H*(*A*, *B*, *C*), (Δ_2) and (Δ_1) are calculated using the followings formulas:

$$\Delta_3 = \begin{vmatrix} \left(\frac{\delta^2 Y}{\delta A^2}\right) & \left(\frac{\delta^2 Y}{\delta B\delta A}\right)^2 & \left(\frac{\delta^2 Y}{\delta C\delta A}\right)^2 \\ \left(\frac{\delta^2 Y}{\delta A\delta B}\right)^2 & \left(\frac{\delta^2 Y}{\delta B^2}\right) & \left(\frac{\delta^2 Y}{\delta C\delta B}\right)^2 \\ \left(\frac{\delta^2 Y}{\delta A\delta C}\right)^2 & \left(\frac{\delta^2 Y}{\delta B\delta C}\right)^2 & \left(\frac{\delta^2 Y}{\delta C^2}\right) \end{vmatrix}$$

$$\Delta_2 = \begin{vmatrix} \left(\frac{\delta^2 Y}{\delta A^2}\right) & \left(\frac{\delta^2 Y}{\delta B\delta A}\right)^2 \\ \left(\frac{\delta^2 Y}{\delta A\delta B}\right)^2 & \left(\frac{\delta^2 Y}{\delta B^2}\right) \end{vmatrix}$$

$$\Delta_1 = \left|\left(\frac{\delta^2 Y}{\delta A^2}\right)\right|$$

The signal of the quadratic coefficients (*e*, *f* and *g*) in the polynomial functions can evidence preliminary initial information about of the indication of maximum and minimum points. If all these coefficients are negative, the function can show a maximum; if all these coefficients are positive, the function can show a minimum; and when some are positive and the others are negative, the critical point can be a saddle point with a relative maximum for the variables with a negative term, and with a relative minimum for the ones with a positive coefficient. Nevertheless, it is always necessary to verify these conclusions by applying the Lagrange criterion.

The coordinates of the critical point (A_c, B_c, C_c) are calculated by solving the equations system: $\delta Y/\delta A = 0$; $\delta Y/\delta B = 0$ and $\delta Y/\delta C = 0$.

The values of the variables found for the critical point are the optimum values and these can be used, in the procedure of the proposed analytical method.

4. Results and discussion

A Doehlert design involving three variables (irradiation time, irradiation power and percentage of H_2O_2) was developed through the 13 experiments (with duplicate in the central point) which are described in Table 2. The recovery (yield of focussed microwave treatment) for each experiment was calculated considering the data obtained in the analysis of the food sample (wheat flour I) by using closed vessel microwave digestion. The irradiation time was varied from 2 to 14 min, irradiation power from 120 to 600 W and volumetric percentage of H_2O_2 in relation to HNO_3 from 10 to 50% (v/v). The experimental results obtained in the Doehlert design, together with the coded and uncoded values for the three variables studied are also shown in Table 2. These data fit in the following functions:

$$\%\mathrm{Ext}\,(\mathrm{Fe}) = 104.33 + 10.47(T) - 25.87(T)^2 + 12.91(P) - 22.48(P)^2 - 0.52(\%\mathrm{H_2O_2}) - 40.66(\%\mathrm{H_2O_2})^2 + 10.50(\mathrm{T})(\mathrm{P}) - 23.69(T)(\%\mathrm{H_2O_2}) - 7.16(P)(\%\mathrm{H_2O_2})$$

$$\%\mathrm{Ext}\,(\mathrm{Zn}) = 100.74 + 21.35(T) - 46.52(T)^2 + 11.89(P) - 16.82(P)^2 + 13.68(\%\mathrm{H_2O_2}) - 15.52(\%\mathrm{H_2O_2})^2 - 13.76(T)(P) - 21.07(T)(\%\mathrm{H_2O_2}) + 11.46(P)(\%\mathrm{H_2O_2})$$

$$\%\mathrm{Ext}\,(\mathrm{Mn}) = 99.65 + 5.98(T) - 18.75(T)^2 + 3.40(P) - 5.70(P)^2 + 2.53(\%\mathrm{H_2O_2}) - 6.17(\%\mathrm{H_2O_2})^2 + 11.44(T)(P) - 2.34(T)(\%\mathrm{H_2O_2}) + 4.09(P)(\%\mathrm{H_2O_2})$$

where %Ext means the recovery obtained by comparing the focussed microwave digestion and closed vessel microwave digestion results for each one element.

These equations illustrate the relations among the three variables and the response. The surfaces, that can be obtained by using STATISTICA software show that all critical values are pertaining at maximums.

The values of $\Delta_1 < 0$, $\Delta_2 > 0$ and $\Delta_3 < 0$ demonstrated that there are points of maximum. This way, the optimum conditions found in coded values were: irradiation time $(T) = 10.4$ min, irradiation power $(P) = 226.8$ W and percentage of H_2O_2 $(\%H_2O_2) = 26.6\%$ for iron; irradiation time $(T) = 9.4$ min, irradiation power (P) = 254.4 W and percentage of H_2O_2 $(\%H_2O_2) = 42.0\%$ for zinc; and irradiation time $(T) = 10.7$ min, irradiation power $(P) = 280.0$ W and percentage of H_2O_2 $(\%H_2O_2) = 40.0\%$ for manganese. In order to establish a single condition that could be useful for the digestion of the samples aiming the determination of all three analytes, working values of T, P and $\%H_2O_2$ were fixed as 12.0 min, 260 W and 42.0% (v/v), respectively. It is important to remark that, at this condition, the experimental model predicts that quantitative extraction of the elements can be achieved. This information is summarized in Table 3.

Table 3
Optimized experimental conditions for Fe, Zn and Mn determinations and working values for multi-elementary analysis

Variable	Fe	Zn	Mn	Worked values
Time (min)	10.4	9.4	10.7	12
Power (W)	226.8	254.4	280.0	260
% v/v H_2O_2 in oxidant mixture	26.6	42.0	40.0	42

Table 4
Results obtained by analysis of certified reference materials employing focussed microwave developed method

Samples	Fe		Zn		Mn	
	CV	FV	CV	FV	CV	FV
Rice flour NIES 10a	12.7 ± 0.7	12.8 ± 0.9	34.7 ± 1.8	35.8 ± 1.0	25.2 ± 0.8	24.9 ± 0.1
Rice flour NIES 10b	13.4 ± 0.9	13.0 ± 0.5	31.5 ± 1.6	32.1 ± 0.9	22.3 ± 0.9	22.5 ± 0.3
Rice flour NIES 10c	11.4 ± 0.8	12.1 ± 0.8	40.1 ± 2.0	41.3 ± 0.7	23.1 ± 0.8	22.9 ± 0.4
Citrus leaves NIST-1572	90 ± 10	92.3 ± 1.0	29 ± 2	29.3 ± 0.7	23 ± 2	24.1 ± 0.8

Results in $\mu g\,g^{-1}$. CV: certified values and FV: found values.

Table 5
Results obtained employing the focussed microwave system developed method and closed vessel microwave system for commercial food samples

Sample	Fe		Zn		Mn	
	FMWS	CVMWS	FMWS	CVMWS	FMWS	CVMWS
Rice flour I	85.0 ± 0.6	81.6 ± 2.3	18.7 ± 0.9	16.4 ± 0.5	8.17 ± 0.46	7.37 ± 0.44
Corn starch I	17.9 ± 0.8	20.2 ± 2.3	3.40 ± 0.93	4.35 ± 0.34	<LOD	<LOD
Oat flour I	51.4 ± 1.5	44.2 ± 0.7	38.2 ± 0.5	38.6 ± 1.0	31.0 ± 0.2	31.2 ± 0.7
Manioc flour	39.5 ± 5.0	40.8 ± 1.8	6.89 ± 0.46	6.12 ± 0.20	3.27 ± 0.06	3.93 ± 1.04
Wheat flour I	22.2 ± 1.5	20.5 ± 3.0	16.9 ± 0.5	17.1 ± 0.1	5.95 ± 0.33	6.28 ± 0.46
Oat flour II	47.4 ± 0.6	53.3 ± 1.2	30.9 ± 0.5	30.7 ± 0.7	38.9 ± 1.0	37.5 ± 0.8
Rice flour II	258 ± 2	238 ± 3	5.50 ± 0.37	5.67 ± 0.98	<LOD	<LOD
Wheat flour II	38.6 ± 4.3	45.0 ± 0.9	19.8 ± 3.8	19.3 ± 1.8	3.66 ± 0.36	4.44 ± 0.75
Corn starch II	28.9 ± 0.6	40.6 ± 5.0	8.11 ± 0.30	11.4 ± 2.4	<LOD	<LOD
Corn flour	14.2 ± 0.7	13.8 ± 2.7	12.1 ± 0.2	14.7 ± 2.6	<LOD	<LOD

Results in $\mu g\,g^{-1}$; FMWS: focussed microwave system; CVMWS: closed vessel microwave system.

5. Evaluation of the method accuracy

The accuracy of the developed procedure was evaluated by the determination of manganese, iron and zinc in certified reference materials supplied by National Institute of Standard and Technology (Gaithersburg, MD, USA): Citrus leaves NIST 1572; and International Atomic Energy Agency (Japan) Rice flour NIES 10-a, 10-b and 10-c. Results are described in Table 4. The statistical comparison by *t*-test showed no significant difference between zinc values obtained from the proposed method and certified values (P-value > 10.46).

6. Analytical application

The procedure optimised was applied for manganese, iron and zinc determination in commercially available food samples. The results were compared with those obtained after closed vessel microwave system digestion. These results are presented in Table 5. Application of paired *t*-test also showed that there is no difference between two methods.

7. Conclusions

The application of a Doehlert matrix became possible, rapid, economical and efficient way of an optimization strategy of the proposed procedure. The focussed microwave assisted digestion procedure developed for the determination of Fe, Zn and Mn in food samples needs no more than 12 min irradiation at 260 W when 10 ml of an oxidant solution containing H_2O_2/HNO_3 (43:57, v/v) is employed, which is a time lower than that required for the conventional closed-vessel microwave methodology.

The method showed good accuracy since no statistical difference was observed from certified values in the analysis of CRMs. Also, when compared with a well-established closed vessel methodology, no statistical difference was observed in the analysis of several commercially available food samples.

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