A New Computational Technique to restrict the Optimal Method for Zinc Determination in a biological sample using Simplex Optimization Method

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Abstract
A computational investigation was used to choose the best acids which gave the real concentration of zinc in biological standard (certified reference material) (C.R.M) known for concentration of zinc. The program was written by using mat lab ver. 7.0. The conditions of the experiment such as (weight specimen, type of acid, dilution of a factor and the response of AAS) were input as a matrix. A computer-run program has used simplex optimization method as a reference base to select the best concentration of zinc.

In this study, the results are represented by one point on the curve (which is related to absolute error as a function of the concentration for each acid) depending on such condition. The point showed that the (HNO_3:H_2O_2) (1:1) is the best mixture for zinc analysis. The computer program showed that it is possible to measure the concentration of another element for different sources and hence different inputs depend on such an experiment using this new program.

Keywords: Simplex, Zinc, Matlab, Computational, Biological.

Introduction
Zinc is an integral component of nearly 300 enzymes in different species of all phyla. It is only secondary to iron in terms of importance as an essential trace element and abundantly present in the body[1-3]. Zinc is significant in biochemical processes, because of playing a vital role in the operation of many enzymes, very important for the stabilization of DNA and gene expression and the transference of a nervous stimulus. In addition to the fact it plays a major role in protein synthesis. It is used in pharmaceutical products such as creams, ointments, eye drops and several types of drugs that fight the infection.

Due to its properties in fighting, the free-radical zinc has been added to the human daily nutrition with vitamins A, B and C[4]. The normal value of zinc in blood serum is 70-120 ug/dl. Since the zinc is an intracellular ion, plasma and serum zinc are not sensitive indicator of depletion[5].

Zinc is as an important element in wound healing. Several studies have proven that it is a vital factor in the biosynthesis and integrity of connective tissue in addition to role the zinc plays during pregnancy and post-pregnancy period[6,7]. It was suggested that the depression of plasma zinc level is one of the major causes of breast cancer and the potential role it plays in tumor growth[8,9]. Different flow injection technique methods have been used to determine the concentration of zinc ion in biological systems such as plasma atomic emission and atomic absorption spectrophotometry[10]. These methods retain high sensitivity and expensive apparatus and do not give significant progress because of the sensitivity or the selectivity when compared to the (dithizone in CCl_4) method[4].

Optimization has been used in analytical chemistry to designate a set of experiments used to find the proper conditions for carrying out a method to achieve the best responses and the best analytical characteristics. The optimum conditions are those that result in better accuracy, higher sensitivity, lower quantification limits, the largest number of measures per time units and lower costs. The costs of the analytical procedure are very important and it is assumed that the best accuracy and the highest sensitivity are the most significant factors to be considered[11]. Optimization processes have been performed by monitoring the influence of one variable at a time on a given experimental response. In this type of optimization, called univariate optimization, when the level of a factor is changed, the levels of other factors of interest are kept at constant values[12].

Matlab is an interactive system in which basic data element is an array that does not require dimensioning. This allows solving many technical computing problems especially those with matrix and vector formulation in a function of the time it would take to write a program in a scalar non-in tractive language such as C or FORTRAN.

Matlab is a high-performance language for technical computing. It integrates computation, visualization and programming in an easy-to-use environment where problems and solutions are expressed in familiar mathematical notation. Typical uses include data analysis, exploration and visualization. Simplex optimization may be applied when all factors are continuous variables; it has been used with success in many areas of analytical chemistry, atomic absorption spectrometry, gas chromatography calorimetric method of analysis, plasma spectrometry and the use of centrifugal analyzer in clinical chemistry. When an instrument is interfaced with a microcomputer, the results of simplex optimization can be wed to initiate improvement in the instrument variables[13-15].

In our study, table 1 exhibits the factors A, B, C, D and E that are used in experiment (a type of acid or its mixture, the response of the atomic absorption spectrophotometer, weight of sample, dilution factor and the absolute error).

Material and Methods

Zinc concentration is measured in certified reference material (C.R.M) type (MA-AI) using many concentrated acids by Flame Atomic Absorption Spectroscopy (FAAS) as illustrated in table 2. The parameter of zinc measured in (C.R.M) such as the concentration of zinc that is obtained from AAS, dilution factor, the weight of the sample and the type of acid input as a matrix. The program has been written with the aid of package (Matlab Ver.7) using simplex optimization method.

Results and Discussion

The sample of the certified reference material (C.R.M) was digested and prepared by using many concentrated acids or its mixture and the zinc concentration in (C.R.M) has been measured using Atomic Absorption Spectrometry (AAS) under the calibration curve:

Abs. = 0.307*conc. (r=0.99163)

With accurate signal and background = 0 for each acid as in fig. 1 Zin Conc. µg/ml.

It was experimentally found that the acid mixture (HNO_3: H_2O_2) (1:1) gave the best result of zinc concentration in (C.R.M) as illustrated in table 2.

The best expression for a real concentration of zinc is given by using the equation of 3rd degree. It has been shown that the 3rd degree equation is the best for investigation about zinc concentration in C.R.M. with the lowest error because the line of the equation represents all the points that deal with a parameter important to detect zinc concentration in the sample. The curve that deals with an error against the zinc concentration has been drawn by three methods (1st, 2nd and 3rd equation) as shown in fig. 2 (a, b and c).

One point resulted from the program running which represents the optimum point for an optimum method for zinc analysis. The point deals with the parameters (type of acid, dilution factor and weight of sample) for zinc analysis which showed that the acid mixture (HNO_3:H_2O_2) (1:1) dilution factor: 25, weight of sample: 0.3 g is the best parameter for zinc analysis which approaches to the parameter obtained from practical method in our study[8,14] as shown in fig 4. The point deals with the parameters (type of acid, dilution factor and weight of sample) for zinc analysis and showed that the acid mixture (HNO_3:H_2O_2) (1:1) dilution factor: 25, weight of sample: 0.3 g is the best parameter for zinc analysis which approaches to the parameter obtained from practical method as shown in fig 3.

Matlab and simplex optimization method program[17] have been written and the parameter (types of acid, dilution factor and weight of sample) were input as a matrix after running; the program gives many new points that deal with the type of acid with another parameter, the new points with absolute error are drawn (practically) as a 3rd degree equation (assuming that it is the best equation) as shown in fig. 4. The results of the practical methods are capable of the result obtained from an experimental method using AAS.[14]

Conclusion

This program has proved successful for finding a suitable method (easily) for investigation about a suitable method with the best parameter that deals with real zinc concentration in biological samples using simplex optimization method only by inserting the parameter used for zinc analysis in a program which was written with the aid of package Matlab.

Table 1
The factors (A, B, C, D and E) deal with the parameters that are used in experiment.

	A	**B**	**C**	**D**	**E**
VERTIX1	A1	B1	C1	D1	E1
VERTIX2	A2	B2	C2	D2	E2
VERTIX3	A3	B3	C3	D3	E3
VERTIX4	A4	B4	C4	D4	E4
VERTIX5	A5	B5	C5	D5	E5
VERTIX6	A6	B6	C6	D6	E6
Sum (excluding vertex 4)	A7	B7	C7	D7	E7
Sum/k (excluding vertex 4)	A8	B8	C8	D8	E8
Rejected vertex (i.e.4)	A9	B9	C9	D9	E9
Displacement =(ii)-(ii)	A10	B10	C10	D10	E10
Vertix7=(ii)+(iv)	A11	B11	C11	D11	E11
VERTIX1	A	B	C	D	E

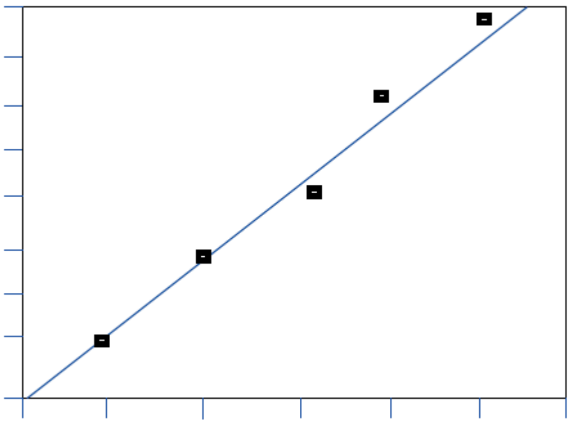

Fig. 1: The line of calibration curve of zinc concent

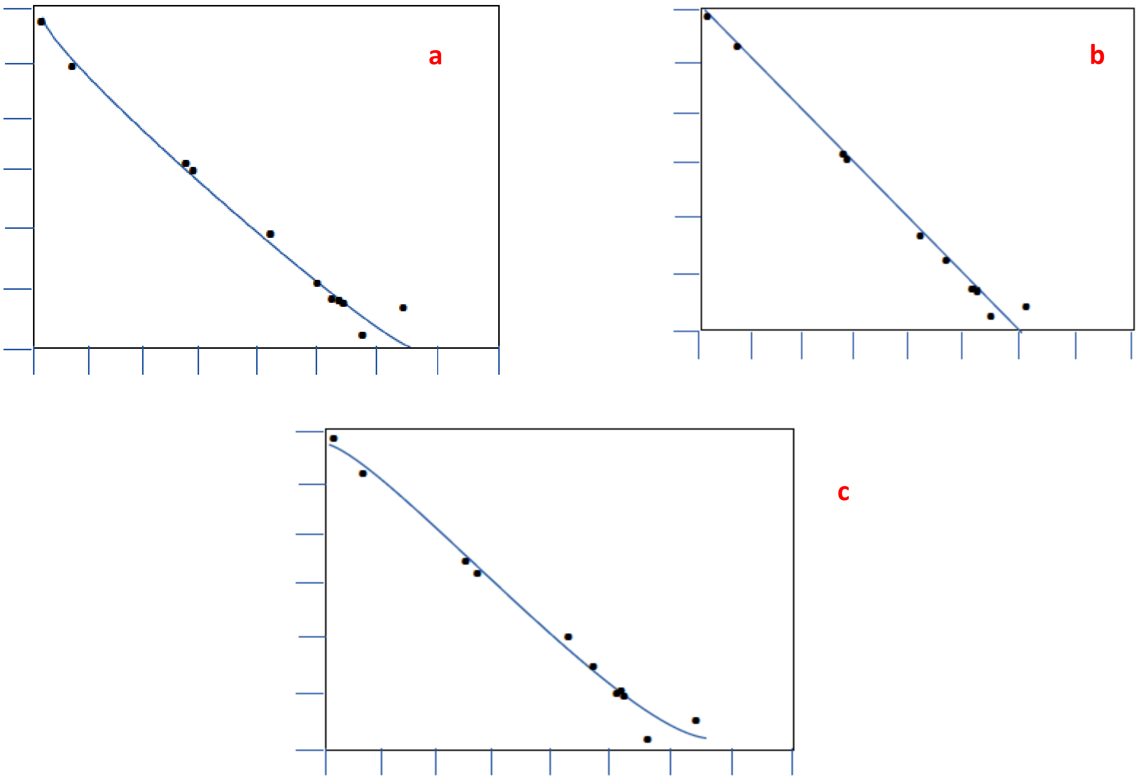

Fig. 2: The curve that deals with an error against the zinc concentration

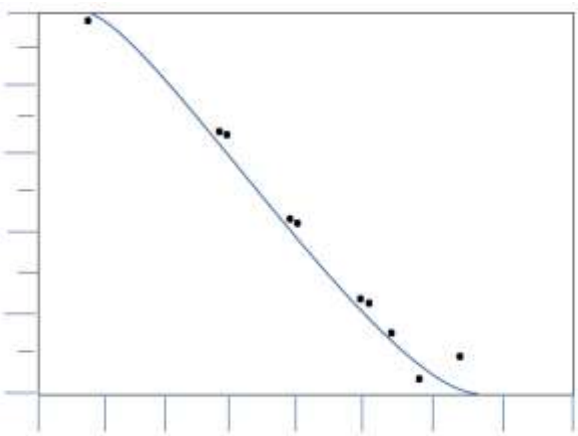

Fig. 3: The optimum point of zinc concentration with lowest error

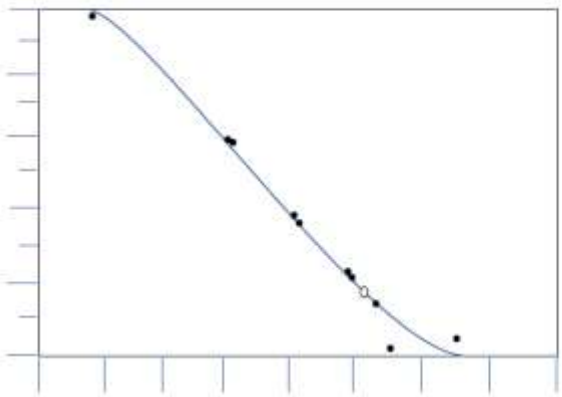

Fig. 4: The optimum point of zinc concentration with the lowest error

Table 2
The concentration of zinc in (C.R.M) obtained from AAS

	Zn conc. C.V=158 (μg.ml^{-1})			
Type of acid or its mixture	**A.V (μg.m^{-1})±sd**	**E**	**E%**	**Rce%±sd**
Conc. HNO_3	126.5±0.60	32.0	20.2	80.06±0.38
(HNO_3:$HClO_4$) (5:1)	150.6±1.47	8.0	5.1	95.31±0.93
(HNO_3:$HClO_4$) (4:1)	163.1±0.35	5.1	3.2	103.2±0.22
(HNO_3:$HClO_4$) (3:1)	127.0±0.65	31	19.6	80.38±0.41
(HNO_3:$HClO_4$) (2:1)	140.1±0.55	17.9	11.3	88.65±0.35
(HNO_3:$HClO_4$) (1:1)	150.5±0.44	7.5	4.7	95.25±0.28
(HNO_3:H_2O_2) (1:1)	156.9±0.15	1.1	0.69	99.31±0.07
($HClO_4$:H_2O_2) (1:1)	108.2±1.26	49.8	31.5	68.50±1.11
(HNO_3:HCl)(4:1)	100.5±0.26	57.5	36.4	63.61±0.17
(HCl:H_2O) (1:1) after ashing at 450˚C	146.5±0.60	11.5	7.28	92.72±0.39
(HNO_3:$HClO_4$) (4:1) after ashing at 450˚C	156.7±0.26	1.3	0.82	99.19±0.20
(HNO_3:H_2O_2) (1:1) after ashing at 450˚C	151.1±085	6.9	4.37	95.64±0.54

C.V=certified value.
A.V=Analytical value
Rec%=Recovery%

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