An Experiment on Sequential Simplex Optimization of an Atomic Absorption Analysis Procedure

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A common situation encountered by analytical chemists is the need to apply or adapt a particular analytical procedure to a new problem. Often this involves determining optimum instrument settings (i.e., those that produce maximum response) and other conditions for the analysis. Optimization may be done using the univariate procedure in which each parameter is systematically and individually varied while all other parameters are held constant. This procedure is usually time-consuming and it does not take account of subtle synergistic effects involving two or more experimental variables.

An alternative to the univariate method is the sequential simplex procedure. By simultaneously varying, according to defined rules, all parameters that affect the magnitude of the analytical signal, the optimum conditions may be estimated. To illustrate and test simplex optimization in a student laboratory is time consuming unless an experiment is chosen in which the variables affecting the response may be readily and rapidly changed. This paper describes a hydride generation atomic absorption experiment using simplex optimization procedures; it is to be carried out in the laboratory with a personal computer near the instrument and requires approximately three hours for completion. The procedures described in this paper have been used to optimize conditions for the analysis of As, Sb, Se, and Bi, but only data for As is reported here.

Hydride Generation Atomic Absorption Spectroscopy

In recent years, hydride generation atomic absorption spectroscopy (HG–AAS) has been widely used for the analysis of elements capable of forming volatile hydrides (As, Sb, Bi, Ge, Pb, Se, Sn, Te, In, and Tl). The method has high sensitivity and is simple, rapid, and relatively free from matrix interferences. Recent reviews (*1*) summarize some of the developments and applications related to the technique.

Hydride generation atomic absorption spectroscopy consists of three separate steps.

1. *Hydride production.* The analyte of interest is converted to its volatile hydride by means of a suitable reducing agent, the most common of which is $NaBH_4$ added as an aqueous solution. Two chemical reactions occur simultaneously—hydride formation and decomposition of the excess reducing agent (*2, 3*).
2. *Transport.* The hydride is introduced into the atomizer either by direct transport with N_2 gas as a carrier or after collection. In the collection mode, the hydride is trapped in liquid N_2 and subsequently re-evaporated into the atomizer.
3. *Atomization.* Atomization usually occurs in a quartz cell that is heated electrically or by flame. The atomization mechanism is complex and may occur partially by direct thermal dissociation, but it also may involve a H free radical mechanism (*4, 5*).

In doing analysis by HG–AAS there are a number of experimental variables that will affect the magnitude of the absorbance signals. Four such variables that can be readily changed and that may have considerably different optimum values for each element are acid concentration in the reaction solution, reaction time prior to sweeping the product into the atomization cell, carrier gas flow rate, and amount of $NaBH_4$ reductant.

Simplex Optimization

The sequential simplex algorithm has been described in a number of review articles (*6–8*). Some useful definitions are as follows:

factor. Experimental variables upon which the response depends.

factor value. The setting or experimental value for a particular factor in a particular experiment.

vertex. Set of n factor values defining a particular experiment.

simplex. An n-dimensional geometric figure composed of $n + 1$ vertexes.

At the start of a simplex optimization procedure, the boundary values for the n factors (for example, the lower and upper feasible limits for experimentation) and response to be optimized must be defined. An initial series of $n + 1$ experiments is then carried out by choosing $n + 1$ vertexes that adequately span the factor space. There are systematic methods to aid in the choice of initial vertexes (*7, 9*). Using results from these experiments, vector algebra is employed to replace the rejected vertex (usually that yielding the poorest response) with a new vertex obtained by reflection of the rejected vertex through the centroid of the remaining hyperface. A new simplex is thus generated and the process repeated until the optimum response is obtained. Modifications to this fixed-size simplex procedure have been made to allow the reflection process to expand or contract (*7, 8*), to cope with selected vertexes which contain values outside the boundaries of a particular experiment (*7*), and to define criteria for the termination of the experiment (*7*).

If a factor value or response lies outside its predefined allowable region, a very poor response is arbitrarily assigned by the user, and the simplex is forced to remain within its defined feasible region.

In order to terminate the optimization process, the user also defines a percentage of domain of each factor level such that, if the length of the reflection for all vertexes is less than the length assigned by these criteria, then the simplexing process stops. Other termination criteria may be applied to indicate that a point of diminishing returns has been reached.

Apparatus

The hydride generation system consists of a three-neck, 125-mL separatory funnel, 1-L polyethylene bottle as an acid reservoir, and an adjustable gas flow meter ⅛ in. with stainless steel float (Lab-Crest Div. F & P Co., Ltd.). These are connected to a heated quartz tube, 1.4-cm i.d. and 14.0-cm length with optical quartz end windows. The cell is held about 1.5 cm above the air–acetylene burner head by an aluminum holder. In this experiment, a Perkin–Elmer 2380 instrument fitted with the appropriate hollow cathode lamps is used. A schematic of the apparatus is shown in Figure 1.

The computer is a Zenith Z-151 PC and the Simplex program is written in Turbo Pascal using the Turbo Graphix Toolbox for screen displays and the Hewlett–Packard HP 7470A Graphics Plotter for plots. Information concerning this program is available on request to the authors.

Reagents

All chemicals used in this experiment are analytical reagent grade or equivalent. A 1000-$\mu g\ mL^{-1}$ As(III) standard solution is prepared by dissolving the appropriate amount of NBS As_2O_3 standard in 5 mL of 10% NaOH solution, then adding 50 mL of water and making up to 250 mL with 10% HCl. Working standards are prepared daily by serial dilution of this standard. Three percent $NaBH_4$ solution is prepared in 0.5% NaOH solution, filtered (Whatman #41 paper) and stored at 4 °C.

Procedure

Boundary conditions are chosen for each experimental variable (Table 1). Five vertexes are then chosen at random from within these boundaries (Vertexes 1–5, Table 2). For analysis under each specific set of conditions, 30 ng of As(III) (300 μL of 100 ppb solution) is injected into the reaction vessel containing 10 mL of aqueous HCl of selected concentration. Nitrogen gas is then passed into the vessel for about 10 s. After the N_2 gas is turned off, the measured amount of $NaBH_4$ is injected and allowed to react for the required time. At the end of this interval N_2 is again turned on at the selected rate to flush the hydride into the quartz cell, and the maximum absorbance is read using a 0.5-s integration time. Each analysis is repeated, and the average value is used in the optimization program. Preliminary experiments had shown no significant difference between results obtained using peak height and peak area.

After responses for the first five vertexes have been measured, the program calculates subsequent factor values, and these are used to determine a new response. This process is repeated until the termination criteria are met, at which time the estimate of optimum conditions is reported.

Table 1. Boundary Conditions

Factor Name	Units	Low Value	High Value
HCl conc	%	5	50
N_2 Flow rate[a]	meter units	5	12
$NaBH_4$ mass	mg	5	40
Reaction time	s	5	60

[a] Actual flow rate ranges from 400 mL min^{-1} (5 meter units) to 1475 mL min^{-1} (12 meter units).

Results and Discussion

Table 2 presents a representative set of factor values and responses obtained from a simplex optimization experiment. The initial factor values were chosen over the entire allowable ranges. Boundary violations occurred for vertexes 6, 8, 12, with the arbitrary poor response of −0.1 causing movement of the new vertex into the acceptable factor region. Vertexes 3 and 4 were retained for five simplexes (i.e., $n + 1$) and thus required that the experiment be repeated using these factor values and the average of the old and new response assigned as the response for the vertexes. This operation, resulting from the "$n + 1$ rule," is invoked in order to ensure that the simplex does not retain an experimental

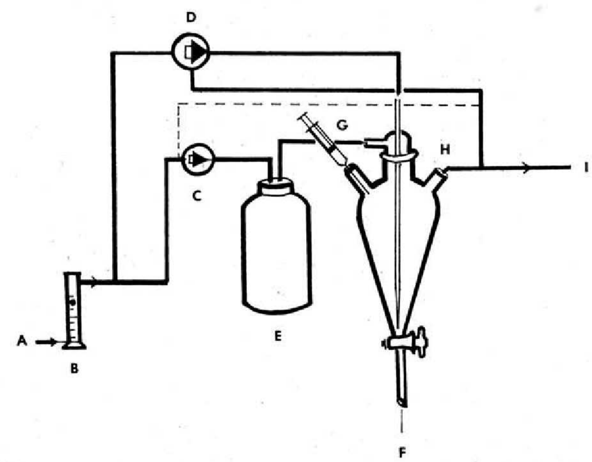

Figure 1. Hydride generation apparatus. A, N_2 gas inlet; B, adjustable gas-flow meter; C, two-way stopcock; D, three-way stopcock; E, acid reservoir; F, reaction vessel; G, syringe for $NaBH_4$ injection; H, sample port (ground glass connection); I, to quartz cell. Dashed line, 1-mm-i.d. polyethylene tubing; solid line, 8-mm-i.d. polyethylene tubing.

Table 2. Simplex Optimization for As Analysis

Vertex number	Simplex number	Vertexes retained[a]	Factor values: HCl conc (%)	N_2 flow rate (meter units)	$NaBH_4$ mass (mg)	Reaction time (s)	Response (absorbance)
1	1		5.0	12.0	10.0	15.0	0.038
2	1		10.0	9.0	5.0	60.0	0.037
3	1		40.0	8.0	15.0	45.0	0.079
4	1		30.0	7.0	20.0	30.0	0.083
5	1		50.0	5.0	10.0	50.0	0.059
6	2	4, 3, 5, 1	52.0	7.0	22.5	10.0	−0.10[b]
7	2		20.6	8.5	9.4	47.5	0.0705
8	3	4, 3, 7, 5	65.3	2.2	17.2	71.2	−0.10[b]
9	3		20.0	9.6	11.8	29.1	0.0735
10	4	4, 3, 9, 7	5.3	11.5	18.1	25.8	0.071
11	5	4, 3, 9, 10	27.1	9.5	23.1	17.4	0.0825
12	6	4, 11, 3, 9	5.3	5.5	16.8	34.9	−0.10[b]
13			27.1	10.0	17.8	28.1	0.084
4[c]	7		30.0	7.0	20.0	30.0	0.086
							0.0845
3[c]	7		40.0	8.0	15.0	45.0	0.081
							0.080
14	7	4, 13, 11, 3	37.1	7.7	26.1	31.2	0.0835
15	8	4, 13, 14, 11	15.8	9.2	28.5	8.3	0.084
16	9	4, 13, 15, 14	23.0	7.4	23.1	31.4	0.084
17[d]	10		25.1	8.5	23.1	24.4	0.088
Optimum by univariate method			20	10	20	30	

[a] Vertexes retained, ranked highest to lowest response.
[b] Boundary condition violation.
[c] Repeat experiment (vertex has been retained for $5(n + 1)$ simplexes).
[d] Last vertex (centroid of last four vertexes retained).

point with an incorrectly measured "high" response (*10*). From Table 2, it is seen that the agreement between the original and remeasured response was good.

The termination criterion (20% for each factor) was satisfied after 16 vertexes, with vertex 17 being calculated by finding the centroid of the hyperface formed by the final four retained vertexes. This final set of factor values was taken to be the optimum.[1] Using a 15% termination criterion, an additional 18 experiments were required to estimate the optimum.

Figure 2a–d plots factor value versus simplex number, with Figure 2e plotting response versus simplex number. The first five points correspond to the initial vertexes. Branches in the graphs indicate that two vertexes were suggested to replace the rejected vertex. The first vertex corresponds to the reflected vertex, the second to the expanded or contracted vertex. The continuous line corresponds to the factor value or response that was retained during the simplex process. The "spikes" reaching the x axis on the plot of response versus simplex number indicate boundary violations, with the response being assigned a value of −0.1.

Table 2 also reports estimated optimum conditions for analysis as determined by the univariate approach. A good agreement between these values and those obtained by the simplex procedure is obtained, and there is similar agreement in corresponding HG-AAS experiments on systems involving Sb, Se, and Bi. Each univariate optimization required approximately 30–50 individual experiments compared with 10–20 in the case of simplex.

[1] Additional methods could be used in order to map the region of the optimum and to determine factor value tolerances needed to ensure that the desired high response is maintained (*7*).

Safety

Each measurement involves 30 ng of As. The use of an efficient extraction hood over the quartz cell should ensure that the TLV of 10 $\mu g\ m^{-3}$ in air is not exceeded.

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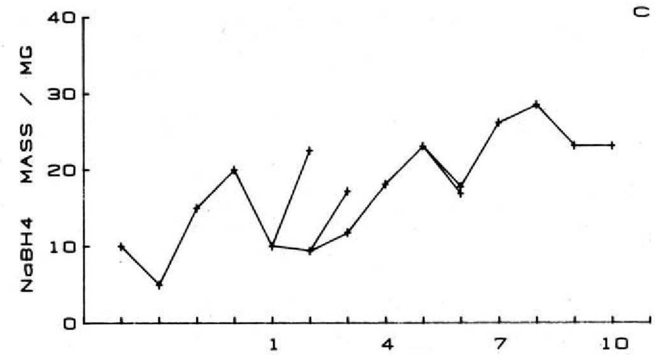

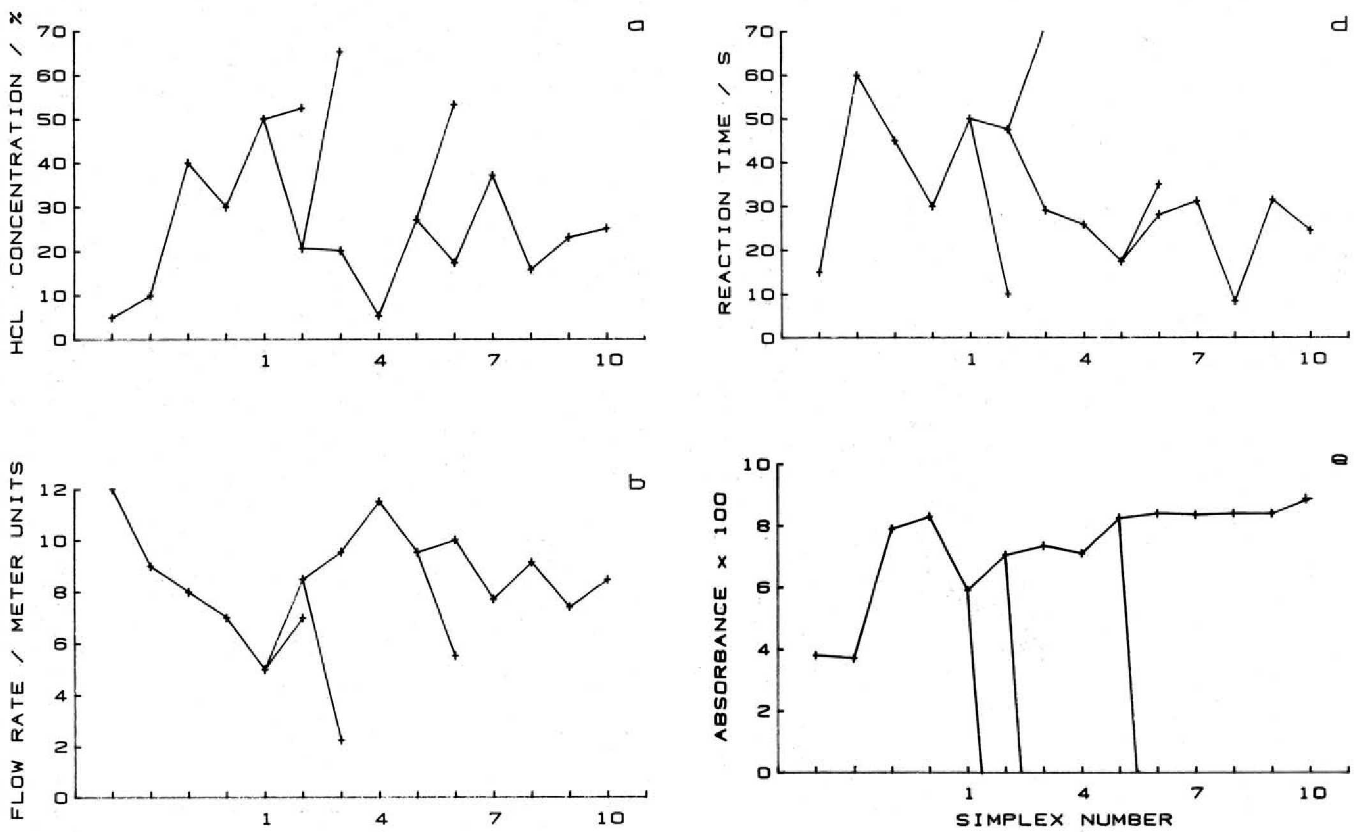

Figure 2. Graphs of factor value or response vs. simplex number; a, HCl concentration; b, N_2 flow rate; c, $NaBH_4$ mass; d, reaction time; e, absorbance.