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SELECTION OF OPERATING CONDITIONS FOR MULTIPLE-ELEMENT ANALYSIS BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY: AN APPLICATION OF OPTIMIZATION METHODOLOGY IN ANALYTICAL CHEMISTRY

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ABSTRACT

Inductively coupled plasma-atomic emission spectrometry can be a particularly effective analytical technique if simultaneous multiple-element determinations can be made with sufficient accuracy and precision.

This report investigates a method of optimizing instrument operating conditions (observation height in the plasma and forward power) for simultaneous multiple-element analysis.

The report heuristically evaluates several objective functions which provide a measure of response. The preferred objective function is then used with the sequential simplex optimization algorithm to select operating conditions for the simultaneous determination of five elements. Experimental results demonstrate the feasibility of this approach.

This optimization method can aid the analyst in selecting instrument operating conditions. Conclusions regarding improvement in system performance/cost effectiveness will depend upon the frequency with which the method specifies operating conditions that improve the analytical capability of the system or that allow simultaneous determinations not possible at the instrument manufacturer's recommended settings.

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Introduction

Analytical laboratories, faced with increased work loads and decreased budgets and personnel ceilings, are seeking ways to minimize personnel time required per analysis, without incurring loss of analytical precision or accuracy. Automated instrumentation such as the commercially available direct-reading polychromators with inductively coupled plasma (ICP) sources (see Appendix A) offer one possible solution to this problem by providing simultaneous, quantitative multiple-element determinations.

Several well known spectroscopists, Winefordner, Fassel, and Boumans among them, have recognized the continuing need for improvement in analytical methods and have compared the performance and cost effectiveness of ICP-atomic emission spectrometry with that of established methods such as flame and electrothermal atomic emission spectrometry, spark atomic emission spectrometry, and x-ray fluorescence spectrometry. Boumans, in his study, used as figures of merit simplicity of instrumentation, cost, precision, multielement capability, freedom from interferences, detection limits, sample handling requirements, and dynamic range. These comparisons have shown that ICP-atomic emission spectrometry is a competitive analytical technique, with the caution, however, that conclusions about a preferred method can be drawn only for situations for which the analytical performance requirements are precisely specified and calculations of cost-to-performance ratios can be made.

Currently, many trace and major element analyses are performed by a variety of sequential methods (e.g. flame and electrothermal atomic absorption spectrometry and spectrophotometry). This means that if a request comes in for determination of five elements on a batch of one hundred samples, each element is determined sequentially on each sample. The benefits of performing these analyses simultaneously -- meaning that all five elements of interest are determined at the same time on a particular sample -- are obvious. Because these multiple-element determinations by ICP-atomic emission spectrometry are the consequence of simultaneous, rather than sequential, measurements of spectral line intensities, a single set of operating conditions must be chosen for polychromator and plasma source.

This report is, then, a feasibility study of a method of optimizing the instrument operating conditions for simultaneous multiple-element analysis by ICP-atomic emission spectrometry. Previously, selection of operating conditions has been accomplished by optimizing one variable at a time, or by simply accepting the instrument manufacturer's recommended settings, although mathematical optimization procedures have been applied to selection of operating conditions for single element determinations. Application of a mathematical optimization procedure to multiple-element determinations requires the definition of an objective function, the selection and implementation of an optimization method, and the experimental verification of results obtained using the objective function and optimization method.

The selection, evaluation and acceptance of an objective function is crucial to solving this problem. The objective function provides a single operative measure of response that is representative of a collection of responses, such as the ratios of line-to-background signals of spectral lines from all elements of interest in a particular sample. Definition of an objective function is of fundamental importance to any empirical optimization technique requiring an evaluation of a response function as part of each experimental cycle. This objective function would thus be used with an appropriate optimization algorithm to select optimum instrument settings. All subsequent samples would then be analyzed at those optimum settings. A low value of the objective function determined from the actual analysis could be used as one parameter to target samples for re-analysis at other operating conditions or by other methods.

Background

The applicability of the sequential simplex optimization method to chemical measurement processes has been clearly demonstrated. Only limited attention has been directed toward an evaluation of a composite response that can be used as an objective function when optimizing instrumental operating conditions for multiple-element determinations.

Such an objective function should reflect a dependence upon the individual concentrations of the elements of interest. The importance of this dependence readily can be understood by considering two multiple-element samples, both of which contain aluminum. In the first sample, if aluminum is present at a concentration three or four orders of magnitude above its detection limit, then the conditions used for the determination of aluminum are relatively unimportant. However, if aluminum is present in the second sample at a concentration only one to ten times its detection limit, then the aluminum concentration becomes a dominant factor in the optimization. The objective function, therefore, should give more significance to the elements of interest which are present at low concentrations relative to their detection limits. This implies that the solution used when performing instrumental operating condition optimizations for simultaneous multiple-element analysis should at least approximately reflect the concentrations of the elements of interest in the sample solutions that are ultimately to be analyzed.

This work defines several possible objective functions which could be optimized through the use of a sequential simplex technique in order to determine observation height and power settings for simultaneous determinations. This work evaluates the performance of these proposed objective functions heuristically and then uses the preferred objective function with the sequential simplex technique to locate optimum instrument settings for the simultaneous determination of five selected elements by ICP-atomic emission spectrometry. Objective function response values, obtained for three arbitrary combinations of observation height and forward power settings, define an initial starting simplex and initiate the optimization procedure. The sequential simplex optimization algorithm (a direct climbing procedure) then specifies the observation height and forward power settings to test until an optimal combination is reached. Problems with the instrument manufacturer's software limited the speed with which this optimization procedure could be carried out, because it was necessary to perform all simplex calculations on a Tektronix 4051 off-line instead of using the Digital Equipment Corporation PDP 11/34 which was interfaced to the instrument. Ideally, however, instrument settings could be adjusted, data collected, an objective function response calculated, and new instrument settings specified in a matter of two or three minutes.

The time-saving advantage of the operating condition selection procedure and the simultaneous multiple element method of analysis used in this work over the currently used sequential methods of analysis (e.g. spectrophotometric, atomic absorption) is obvious and substantial. This work demonstrates the feasibility of using the proposed objective function and a sequential simplex search to locate optimal operating conditions. Studies in progress at the U.S. Geological Survey will determine the effectiveness of this search technique and the proposed objective function in achieving time-saving or analytical advantages over alternative methods of selecting operating conditions (use of the instrument manufacturer's recommended operating conditions or use of univariate or random searches).

The Objective Function

Methods of experimental optimization, including the sequential simplex, rely upon a clearly defined objective function which must be evaluated after each trial.

In the past, the most common multiple-element optimization method has been to find the conditions that give the optimum response for each individual element of interest and then to select a compromise set of operating conditions (1-4). Greenfield and Burns (5) discussed several figures of merit which could be optimized in order to compare the performance of argon-cooled and nitrogen-cooled plasma torches. Using an alternating variable search method, they optimized the net signal to net background ratio. However, they also only worked with emission lines of individual elements. Wegscheider, Jablonski, and Leyden (6) considered various objective functions for use in multiple-element analysis by X-ray fluorescence and concluded that objective functions could be derived which closely resembled the qualities intrinsically sought by X-ray spectroscopists. One such function which gave an overall measure of precision was

$$Y_2 = \frac{1}{t_r} \prod_{i=1}^{n} \frac{I_{i,p} - I_{i,b}}{C_i\sqrt{I_{i,p} + I_{i,b}}} \quad \text{for } (I_{i,p} - I_{i,b}) > (2.71 + 4.65\sqrt{I_{i,b}})$$

and $Y_2 = 0$ otherwise, where

t_r = real time needed to acquire a spectrum

n = number of elements of interest

$I_{i,p}$ = gross intensity of element i

$I_{i,b}$ = background of element

c_i = the concentration of element i

Morgan _et al._(7) successfully used the sequential simplex method to optimize multiple-component chromatographic separations. A chromatographic response function (CRF) based on peak separation was used as an operational measure of performance:

$$CRF = \sum_{i=1}^{j} \log_e (P_i)$$

where P_i = depth of the valley below a straight line connecting two adjacent peak maxima divided by the height of the straight line above the baseline at the valley of the i-th pair pair of adjacent peaks

Ebdon _et al._ (8) compared the analytical performance of nitrogen-cooled and argon-cooled plasmas for single element determinations following preliminary optimization by the sequential simplex method.

This work defines several possible objective functions for use in multiple-element determinations by ICP-atomic emission spectrometry. The performance of a proposed objective function is described and evaluated in the Results and Conclusions section.

Because it is a measure of merit which is easily evaluated, the net spectral line signal to spectral background ratio, as defined by equation I, is used throughout this work.

$$(S/B) = \frac{\text{Total Signal-Background}}{\text{Background}} \qquad \text{I}$$

Obviously, the signal-to-noise ratio would be another possible figure of merit to measure.

It is important in the determination of compromise conditions for multiple-element analyses that the objective function generated provide greatest sensitivity for elements with the smallest (S/B) ratio and that it provide progressively less sensitivity as the (S/B) ratio increases. Initially, it appeared that a two-term function, such as that given in equation II, might be appropriate.

$$F = (S/B)^m + k \left[\frac{(S/B)_{min}}{(S/B)_{max}} \right]^n \qquad \text{II}$$

where m, n, and k are constants, and min and max designate the minimum and maximum signal-to-background ratios for the lines of interest. The first term of this function focuses specifically on the line with the smallest signal to background ratio. The second term introduces a uniformity criterion; that is, it can increase the value of the objective function by discriminating in favor of $(S/B)_{min}$ at the expense of $(S/B)_{max}$. A rather obvious shortcoming of this function is that it requires the evaluation of the three constants k, m, and n. A second and far more subtle problem was discovered while using this function to generate responses from experimental data. Because an ICP direct reading polychromator with similar response photomultiplier tubes was used, $(S/B)_{min}$ and $(S/B)_{max}$ could very closely approach one another in the absence of sample. This latter condition caused the objective function, F, to range from zero to infinity when sample was present, but to give a response approaching k when sample was absent. Because of these problems, other objective functions were investigated.

The general weighted average (Equation III) appears to have all the features of an acceptable objective function.

$$F = \frac{\sum_{i=1}^{n} W_i \, (S/B)_i}{\sum_{i=1}^{n} W_i} \qquad \text{III}$$

where w_i is the weight assigned to the corresponding (S/B) ratio. In a trivial case, this function reduces to the minimum (S/B) ratio if $W_i = W_2 = \ldots = W_{min-i} = W_{min+i} = W_n = 0$ and $W_{min} = 1$. The function reduces to a simple average if $W_i = W_2 = \ldots = W_n$. These weighting functions were investigated, as were those of the form $W_i = e^{-(S/B)_i}$ and $W_i = (S/B)_i^{-N}$, where e is the base of the natural logarithm and N is a constant.

Selection of an objective function, at this point, might appear arbitrary; this is not totally the case. In X-ray fluorescence or radiochemistry, where the experimental uncertainty can be estimated via counting statistics; a theoretically based objective function is possible, whereas in emission spectrometry, as in the case of multi-component chromatographic separations, an objective function must still be selected intuitively. Table I illustrates this intuitive selection process. The first three columns in Table I present five sets of simulated (S/B) ratios for three atomic emission lines. Overall, the five sets of data are arranged in decreasing order of desirability; therefore, the values of the objective function should follow this trend. The last seven columns correspond to the values of the objective function (III) for the weights indicated. Only the data in column D, $W_i = (S/B)_i^{-1.0}$, monotonically decreases, indicating that weighting with the reciprocal of (S/B) agrees with our *a priori* views.

A simple example using two sets of (S/B) ratios with the same arithmetic mean (X) is algebraically represented in Table II. In the second set, however, one ratio is displaced Z units above X while the other has a ratio displaced Z units below X. The last column summarizes the value of the weighted-average objective function where $W_i = (S/B)_i^{-1.0}$ in each case. Since the (S/B) ratio must be greater than zero, $X^2-(Z^2/X)$ must always be less than X, indicating that the uniformity criterion is implicit in this function.

Thus, weighting with the reciprocal of $(S/B)_i$ agrees with our *a priori* views, and our proposed objective function simplifies to equation IV if $W_i = (S/B)_i^{-1}$

$$F = \frac{n}{\sum_{i=1}^{n} (S/B)_i^{-1.0}} \qquad \text{IV}$$

Table 1. Illustration of selection process for an objective function.

Signal to-background ratio			Values of objective function III for different weighting factors*						
$(S/B)_1$	$(S/B)_2$	$(S/B)_3$	A	B	C	D	E	F	G
2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.200	1.000	10.000	0.200	3.73	1.29	0.492	0.291	0.235	0.532
0.100	5.000	5.000	0.100	3.37	1.18	0.288	0.128	0.104	0.171
0.100	1.000	10.000	0.100	3.70	1.00	0.270	0.137	0.110	0.361

*A = Min $(W_1 = W_2 = W_{min-1} = W_{min+1} = \ldots = W_n = 0 \text{ and } W_{min} = 1)$

B = Average $(W_1 = W_2 = W_1 = \ldots = W_n)$

C = $W_i = (S/B)_i^{-0.5}$

D = $W_i = (S/B)_i^{-1.0}$

E = $W_i = (S/B)_i^{-1.5}$

F = $W_i = (S/B)_i^{-2.0}$

G = $W_i = e^{-(S/B)_i}$

Table II. Illustration of the uniformity criterion.

Set No.	$(S/B)_1$	$(S/B)_2$	Objective Function IV
1	X	X	X
2	X + Z	X - Z	$X - Z^2/X$

The Sequential Simplex Algorithm

The applicability of empirical optimization techniques to chemical processes was demonstrated by Box (9) in 1951 when he introduced the Box-Wilson "approach to the optimum" technique. Later, Box, advocated a simplified version of this "steepest ascent" procedure, an experimental optimization technique which he called "evolutionary operation" (10) for improving established industrial or chemical processs. In applying this technique, a systematic cycle of variants of the current chemical process was explored until an indication of desirable change emerged. The process was then modified in the indicated favorable direction. The procedure, however, did not specify rules on either when to change or how to change the process.

Spendley et al. (11) in 1962 developed the sequential simplex optimization method in an effort to automate the evolutionary procedure. The method depended upon comparison of function values of the vertices of a simplex, followed by replacement of the vertex with the worst value by another point. Calculations were rigidly specified, yet simple enough to be easily automated.

Brooks (12) compared the performance of several optimum seeking methods for which the functional relation between the response and the variables was unknown. Factorial designs, univariate procedures, methods of steepest ascent, and random experimentation were compared on the basis of the magnitude of the response at the estimate of the optimal variable combination resulting from application of the methods for a fixed number of trials. On this basis, the slope method of steepest ascent performed better than the other methods considered.

Using the same response surfaces as Brooks, and as far as possible the same experimental regions, Spendley et al. made similar comparisons of the performance of the sequential simplex optimization method. These simulations showed that by virtue of its performance (only the slope method of steepest ascent was clearly better) and its simplicity, the sequential simplex technique was a useful optimization method.

Long (13) successfully applied the theoretical proposal of simplex optimization to two analytical chemistry procedures, the ρ-rosaniline method for determination of sulfur dioxide and the molybdenum-blue method for determination of phosphate.

Since its introduction in 1962, the simplex optimization procedure has undergone several modifications. A modification by Nelder and Mead (14) of the simplex method allowed acceleration in directions that were favorable and deceleration in directions that were unfavorable. King (15) modified the Nelder and Mead algorithm to allow for failed contractions (decelerations). Yarbro and Deming (16) discussed selection of variables, initial step size, and initial vertices. Routh et al. (17) suggested the use of second-order polynomials to locate the position of the new vertex. However, this had the disadvantage of significantly increasing the programming effort required. Ryan et al. (18) proposed a "controlled weighted centroid" method and an "orthogonal jump weighted centroid" method, both of which more closely approximated the gradient direction than did the Nelder and Mead algorithm. Although both of these weighted centroid methods did find the neighborhood of the optimum more rapidly than did the Nelder and Mead algorithm, they were less efficient when forced to determine the optimum point itself.

The sequential simplex optimization method has been applied in recent years to many areas of chemical research and instrument design, including, but not limited to the study of pulsed hollow cathode lamp performance (19), preparation and operation of microwave excited electrodeless discharge lamps (20), flame atomic absorption (21), and energy dispersive X-ray spectrometry (22), and gas-liquid chromatographic methods. The method has proven to be an efficient and conceptually simple technique for improvement of response in chemical applications.

This work applies the sequential simplex method to the selection of optimal compromise operating conditions for the simultaneous determination of five elements by inductively coupled plasma-atomic emission spectrometry. The algorithm used is based on the King modification of the Nelder and Mead algorithm.

The variable-size sequential simplex algorithm of Nelder and Mead consists of reflection, expansion, and contraction rules. It is useable with any number of variables and is applicable to minimization as well as maximization of response. A two variable maximization problem will be used to illustrate the process (see Fig. 1). For the current work, these variables are observation height in the plasma and forward power.

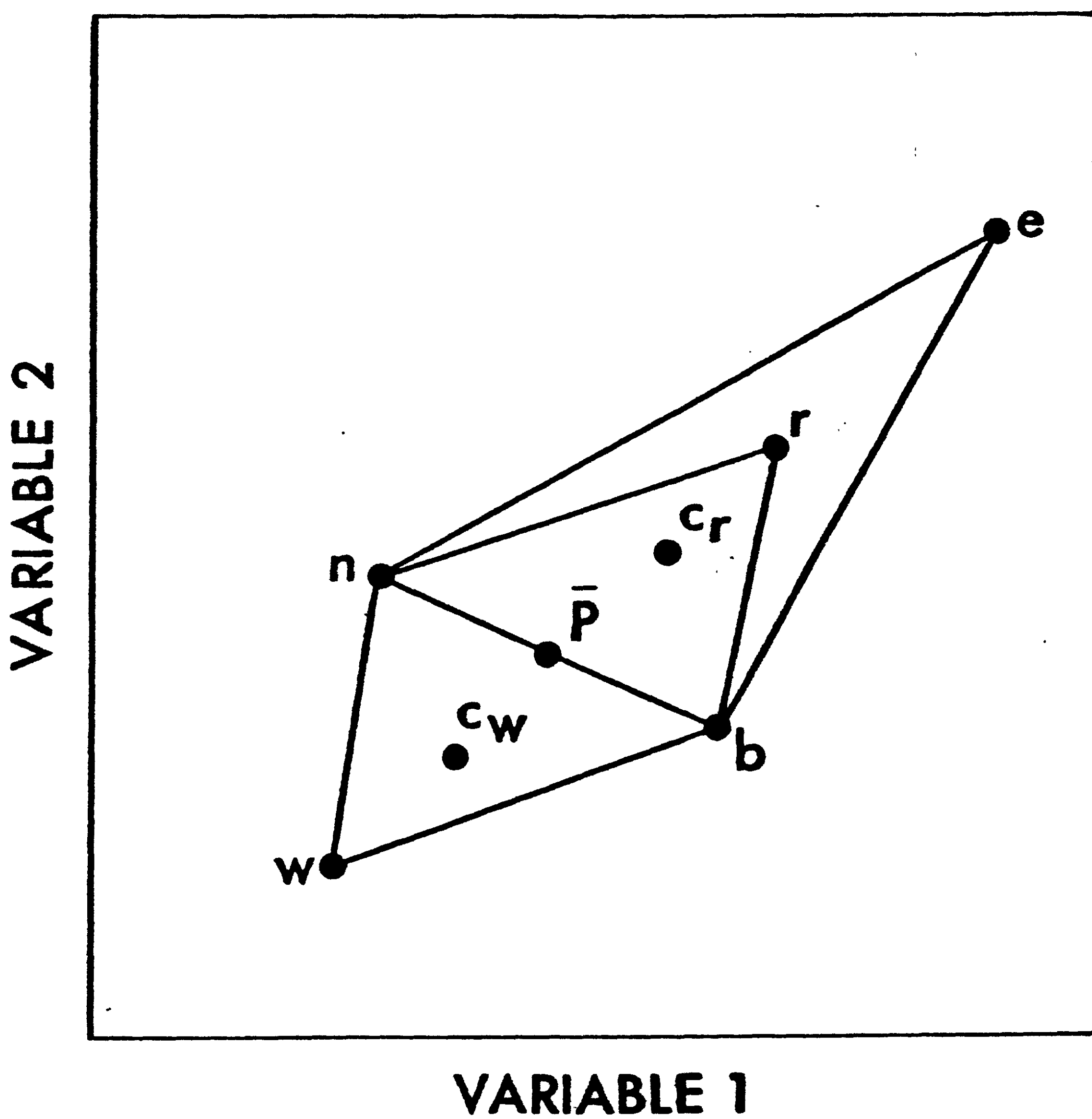

Figure 1. Two variable simplex.

In the initial simplex, w, n, and b correspond to the responses at the vertices with the worst (W), next-to-worst (N) and best (B) responses. $\overline{P}$ is the centroid of the simplex calculated without W. r represents the response at the vertex associated with the reflection, R, which is accomplished by extending the line segment $\overline{WP}$ beyond $\overline{P}$ to the new vertex R, where

$$R = \overline{P} + (\overline{P} - W)$$

If the response at R is better than that at B, an expansion is attempted by extending the line segment $\overline{WR}$ to the new vertex E, where

$$E = \overline{P} + 2\ (\overline{P} - W)$$

and e represents the response at the vertex E. According to the expansion rules of Nelder and Mead, as stated by Shavers _et al._ (23): "If the response at E is better than the response at B, E is retained and the new simplex is NBE. If the response at E is not better than at B the expansion is said to have failed and BNR is taken as the new simplex". King modified the expansion rule of Nelder and Mead by comparing the response at E to the response at R, rather than that at B.

Although this modification appears to improve the rate of convergence of the simplex, it was not discussed in an _Analytical Chemistry_ review article by Deming _et al._ (24). Explicit use of this modification appears to be limited to an engineering application by Dowson _et al_. (25).

In Fig. 1, c_R and c_W represent responses at the contracted vertices C_R and C_W. Shavers et al. stated the contraction rules of Nelder and Mead as follows: "If the response at R is worse than the response at N, but not worse than at W, the new vertex should be closer to R than to W:

$$C_R = \overline{P} + 0.5\ (\overline{P} - \overline{W})$$

The process is restarted with the new simplex BNC_R. If the response at R is worse than the response at W, the new vertex should lie closer to W than to R:

$$C_W = \overline{P} - 0.5\ (\overline{P} - \overline{W})$$

The process is restarted with the new simplex BNC_W." A contraction fails if the response at C_R is worse than that at R, or if the response at C_W is worse than that at W and results in a massive contraction in which the size of the simplex is further reduced.

King suggested the following modification which was used by Morgan and Deming in their chromatography work: "If the contraction vertex is the worst vertex in the new simplex, do not reject that vertex, but instead the next-to-worst vertex, N".

It was not apparent at this point whether, in the event of a failed contraction, the contracted vertex was always to be retained or was to be retained only if the response at the contracted vertex was better than that at both R and W. This ambiguity led to the incorporation of the following contraction modifications. The C_R contraction rule was modified so that the response at the contracted vertex, C_R, was compared with the response at R. The vertex C_R was retained only if the response at C_R was better than that at R. The C_W contraction rule was modified in a similar manner, so that the contracted vertex, C_W, was retained only if the response at C_W was better than that at W.

Because the overall effect of these modifications is to slow the size-variation of the simplex without altering the directional movement, these modifications may reduce the likelihood of aimless wandering of the simplex in response to noise and thereby improve the efficiency of the algorithm in the presence of noise as well. No comparison was made, however, of the performance of the modified and unmodified algorithms under experimental conditions.

When the Nelder and Mead algorithm is used on responses subject to error, the simplices may retain a false high result as though it were a true optimum. Therefore, if a vertex has been retained in (k+1) successive simplices (where k equals the number of variables), the response at the persistent vertex should be re-evaluated and the results should be averaged with previous observations. Less difficulty is caused by false low results, as these vertices will be quickly eliminated through application of the algorithm rules.

If a new vertex lies outside the boundaries of the independent variables, it may be assigned an undesirable response to force the simplex back inside its boundaries. Alternatively, a C_W contraction may be performed to generate a new vertex lying between W and P. This latter approach was used in this work.

Because very often little is known about the response surface of the chemical system under investigation, it is difficult to establish response and variable termination criteria for the simplex search. Suggested approaches have included halting the search when the simplex step size becomes less than some predetermined value, when the differences in response approach the value of the indeterminate error, or when some predetermined number of iterations has been performed. In this work, the simplex was allowed to continue until the forward power and observation height coordinates converged to within the precision with which they could be adjusted.

A flow chart of the algorithm and computer programs in BASIC and in Fortran are presented in Appendix B.

Experimental Measurements

Throughout this work a Jarrell-Ash Mark III, a direct-reading polychromator with an argon plasma source, was used. A nebulizer flow of 0.55 L min^{-1} of argon and a coolant gas flow of 17.0 L min^{-1} of argon were maintained. A signal integration time of two seconds was used for both peak and background measurements. The background for each line was selected at 10 spectrum shifter units (approximately 0.032 nm) to the high wavelength side of each spectral line peak. Observation height above the upper loop of the coupling coil and forward power ranged from 7 to 27 mm and from 700 to 1900 watts, respectively. Prior to each determination, the reflected power was set to a minimum ($\leq$ 3 watts) while the sample solution was aspirated (sample uptake rate = 1.0 mL min^{-1}).

A stock solution was prepared from Fisher certified aluminum, manganese, sodium and titanium 1000 μg mL^{-1} atomic absorption standards and Spex Industries phosphorus 997 μg mL^{-1} atomic absorption standard. The emission lines and concentrations were: Al I 396.152 nm, 6 μg mL^{-1}; Na I 588.995 nm, 2 μg mL^{-1}; Ti II 334.941 nm, 40 ng mL^{-1}; P I 214.914 nm, 1 μg mL^{-1}. For this solution to better reflect the properties of the real samples that frequently are dissolved in HF or other acids, the following reagents were added: 4 mL (28.9 M) hydrofluoric acid, 2 mL (12.1 M) hydrochloric acid, 1 mL (15.9 M) nitric acid and 1g H_3BO_3 per 100 mL of stock solution. Under the operating conditions selected, Al was present at approximately 1000 times its detection limit, P was present at approximately 10 times its detection limit, and Na, Mn, and Ti were present at approximately

100 times their detection limits which were determined at 1100 watts forward power and at an observation height 16 mm above the coil (power and location suggested by instrument manufacturer). These elements, lines and concentrations were selected because they encompass a variety of conditions commonly associated with the analysis of geological samples.

Spectral line intensity data were acquired using a Jarrell Ash Mark III ICP. Data were recorded and processed using a Digital Equipment Company PDP 11/34 minicomputer with 64K words of memory and dual RL01 disk drives which was interfaced to the spectrometer. All simplex calculations were performed off-line using a BASIC language program on a Tektronix 4051 microcomputer.

Results and Conclusions

Objective functions have been described for use in multiple-element determinations by X-ray fluorescence spectrometry and for use in multiple-component chromatographic separations. This work describes an objective function for use in multiple-element determinations by atomic emission spectrometry. The objective function is then used with the sequential simplex optimization method to select optimal forward power and observation height settings for multiple-element determinations by ICP-atomic emission spectrometry. The sequential simplex optimization method was chosen because of its simplicity and its proven effectiveness in chemical applications where the functional relationship between response and variables is usually unknown.

Table III summarizes the forward power, observation height, individual (S/B) ratios for each of five spectral lines, and the value of the objective function (equation IV, $F = \frac{n}{\sum_{i=1}^{n} (S/B)_i^{-1}}$) for each instrument setting tested. The simplex was allowed to move until the forward power and observation height coordinates had converged to within the precision with which they could be adjusted (20 watts for forward power and .20 mm for observation height). The asterisks indicate that random noise caused the background (B) to exceed the line intensity signal(S) for the designated spectral line. Whenever this happened (vertices 2, 8, and 12 in Table III), the corresponding (S/B) ratio and the objective function were assigned very unfavorable values. Vertices 13, 17, and 22 in Table III illustrate the retention of a vertex having a high response. The response at this retained vertex was periodically reevaluated and averaged with previous observations, resulting in an objective function value of 0.852 for an observation height of 14.0 mm and forward power of 1220 watts. Had the initial high response at vertex 13 been due to noise, the vertex probably would have been eliminated from the simplex when it was reevaluated. Once the optimum had been located (1220 watts and 14.5 mm), ten replicate determinations of the objective function at those settings provided a response of 0.802 $\pm$ 0.032 units. The convergence criterion used in this experiment was the precision with which forward power and observation height could be adjusted. It was, therefore, relatively unimportant whether the optimum setting was considered to be the best point of the final simplex (1200 watts and 14.3 mm) or the center or average of the final simplex (1220 watts and 14.5 mm).

The data and results in Table III are based on printout from optimization calculations performed off-line (see Appendix C). Table III indicates that the last simplex would not correspond to the best conditions for any single element. For example, a lower power and higher observation height setting such as the 1050 watts and 17.7 mm used at vertex 10 would have been better for an Al determination. Examination of the individual elemental S/B ratios indicates, however, that these conditions provide a very realistic compromise when determining the five selected elements in the concentration regions specified.

At present, the value of the proposed objective function at the optimal instrument operating conditions is of importance only in that it specifies a preferred combination of settings relative to other settings tested. Software modifications could be made, though, to indicate low elemental S/B ratios and to suggest the possibility of deleting the corresponding element or elements from the optimization procedure. During actual sample analysis, however, interest centers on the individual S/B ratios and information concerning noise. This information, not the proposed objective function, dictates whether a particular sample should be reanalyzed for a particular element.

The data in Table III and Appendix C show that the proposed objective function specifies an optimal setting which is in agreement with our *a priori* views concerning a preferred combination of S/B ratios for the five elements being determined. The relatively low S/B ratios of Ti and P are improved at the expense of the Al, Na, and Mn S/B ratios. Additional experimentation was not done to verify the location of the optimum because the region of the simplex search included the instrument manufacturer's recommended settings (1100 watts and 16 mm for determination of any element or combination of elements in aqueous solution) and published recommended settings for the individual elements determined. Under different circumstances, the simplex algorithm could have been started from several locations to see whether it converged to the same point. Factorial designs and univariate searches could also have been used to verify the optimum.

Thus, this work has demonstrated the feasibility of using the proposed objective function in conjunction with a variable-size sequential simplex algorithm to optimize operating conditions for simultaneous determination of five selected elements by ICP-atomic emission spectrometry. Although this search method can aid the analyst in locating optimal operating conditions, its usefulness in actual sample analysis will depend upon the frequency with which it specifies optimal operating conditions that improve the analytical capability of the system or that allow simultaneous determinations not possible at the instrument manufacturer's recommended settings. The search method described is general and subsequent work will expand this approach to a multiple-variable optimization (observation height, forward power, nebulizer gas flow, coolant gas flow, concentration of an ionization suppressing element, e.g. Cs) which is expected to facilitate the determination of major, minor, and trace elements in silicate rocks and minerals of geochemical interest.

Table III. Experimental data illustrating use of objective function IV.

Simplex Vertex #	Forward Power (watts)	Observation Height (mm)	S/B Ratios of Individual Elements in Standard Solution Al	Na	Ti	P	Mn	Objective Function Value
1	800	8.0	2.24	2.44	0.04	0.17	0.07	0.104
2	1250	25.0	7.24	2.64	0.75	*	0.77	*
3	1700	8.0	2.17	1.50	0.03	0.32	0.16	0.106
4	1250	16.5	12.51	2.66	0.53	0.18	2.00	0.598
5	1140	10.1	7.32	2.76	0.09	0.34	0.38	0.299
6	1450	10.7	4.96	2.06	0.14	0.32	0.51	0.381
7	1250	16.5	12.70	2.47	0.56	0.24	1.76	0.708
8	1560	17.0	6.83	1.58	0.41	*	1.63	*
9	1240	11.9	8.01	2.53	0.20	0.95	0.71	0.624
10	1050	17.7	17.28	2.86	0.71	0.14	1.44	0.514
11	1150	15.9	14.90	2.83	0.50	0.29	1.50	0.766
12	1150	20.6	15.05	2.85	0.76	*	1.50	*
13	1220	14.0	11.48	2.62	0.41	0.50	1.32	0.877
14	1120	13.5	12.15	2.74	0.36	0.45	0.97	0.767
15	1190	11.6	8.85	2.83	0.17	0.48	0.60	0.503
16	1160	14.8	13.04	2.83	0.46	0.36	1.34	0.821
17	1220	14.0	12.04	2.88	0.40	0.52	1.25	0.884
18	1260	15.4	11.83	2.60	0.48	0.30	1.60	0.763
19	1150	14.0	12.38	2.79	0.38	0.40	1.14	0.782
20	1220	13.1	10.49	2.72	0.32	0.45	1.04	0.744
21	1200	13.6	11.60	2.87	0.36	0.44	1.13	0.784
22	1220	14.0	10.77	2.35	0.40	0.44	1.29	0.852
23	1270	13.6	10.13	2.63	0.34	0.44	1.18	0.758
24	1180	13.9	12.03	2.99	0.37	0.43	1.16	0.788
25	1200	14.3	12.08	2.70	0.43	0.43	1.39	0.857
26	1200	14.7	12.41	2.84	0.43	0.37	1.39	0.811
27	1240	14.5	11.75	2.71	0.42	0.38	1.35	0.802

* indicates background exceeded signal

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Appendix A

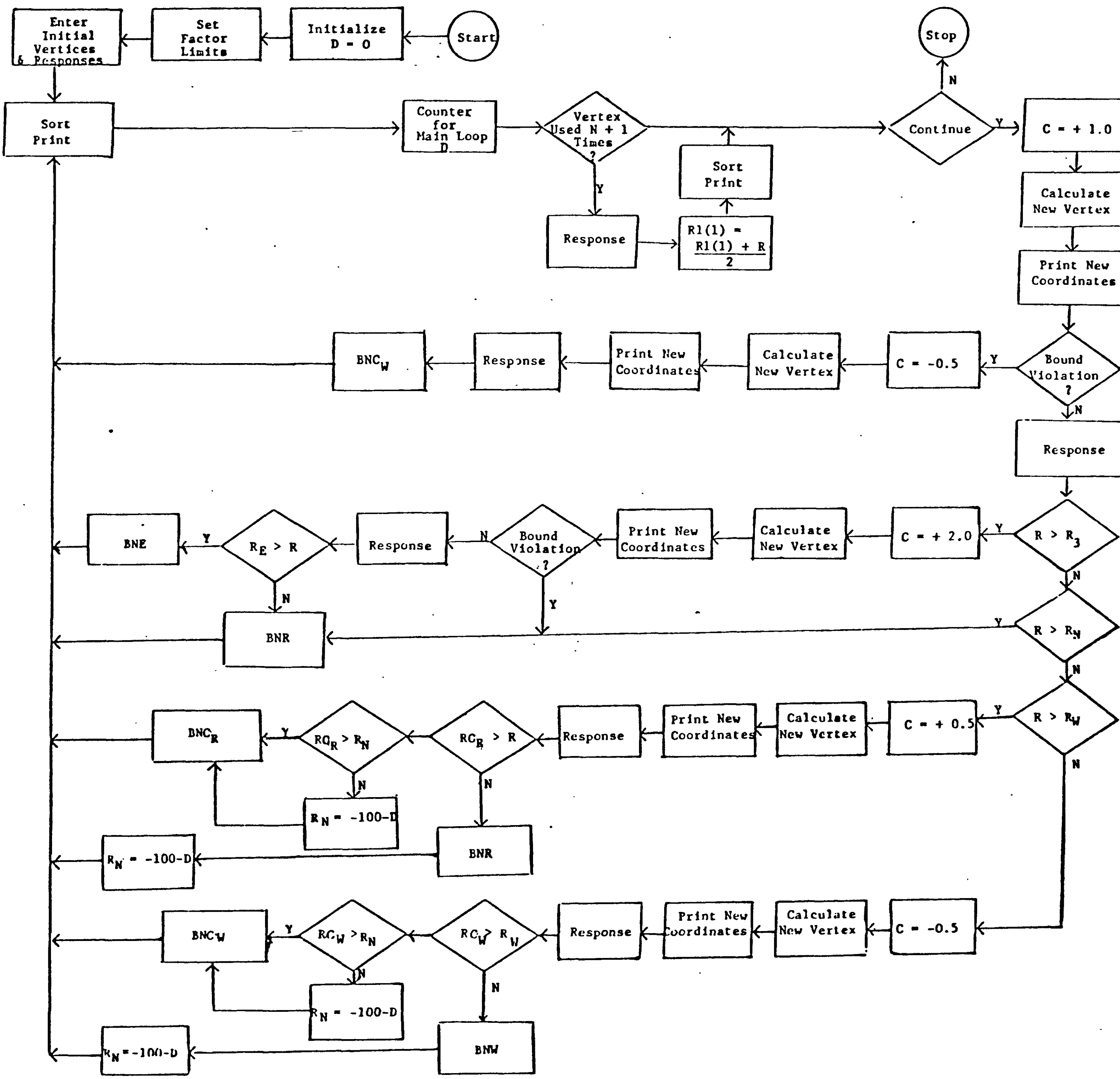
Brief Description of Inductively Coupled Plasma-Atomic Emission Spectrometry

Brief Description of Inductively Coupled Plasma-Atomic Emission Spectrometry

In ICP-atomic emission spectrometry, a radio frequency (RF) generator provides energy to a plasma torch and creates an RF magnetic field. Argon gas is passed through the field and is ionized to become the plasma. Sample solution is aspirated from a container and carried by another stream of argon gas to the plasma discharge, where excitation occurs. Excited elements emit photons of light which are directed by the optical system through an entrance slit onto a concave grating surface. The grating diffracts the light into its component wavelengths which are focussed to form images of the entrance slit on a focal curve. Exit slits isolate wavelengths of interest. Photomultiplier tubes behind these exit slits convert light to electrical energy proportional to the intensity of the spectral lines. A computer then converts these signals into desired concentration units and prints or displays the results. The location and magnitude of these emission signals and the noise from sample and discharge gas are influenced by physical properties of the plasma discharge. These properties are in turn controlled by the operating characteristics of the instrument system. Among the critical parameters for analysis are the power input to the discharge and the observation region in the plasma. Selection of these operating conditions affects the limits of detection for simultaneous multiple-element analysis.

Appendix B

Flow Chart of Sequential Simplex Algorithm and BASIC and Fortran Programs



Flow Chart of Sequential Simplex Algorithm

Sequential Simplex Program in BASIC

```
100 REM J = VERTEX #
110 REM I = FACTOR #
120 PRINT "# OF DIMENSIONS = ";
122 INPUT N
124 PRINT "# OF LINES = ";
125 INPUT M
127 PRINT "POWER TO BE USED IN WEIGHTING FUNCTION -- RESPONSE SUB = ";
128 INPUT W7
130 DIM L(10),H(10),R1(10),V(10),V1(10,10),V2(10),V3(10)
131 DIM V4(10),V5(10),S8(20),B8(20)
132 DIM W(100),W1(100,6)
133 DIM R0(20)
140 REM FOLLOWING LOOP SETS LIMITS FOR N DIMENSIONS
150 FOR I=1 TO N
160 READ L(I),H(I)
170 NEXT I
172 D=0
180 DATA 700,1900
190 DATA 7,27
200 REM NEXT SET OF LOOPS INITIALIZE FIRST SIMPLEX
204 PRINT
205 PRINT "INITIAL SIMPLEX"
210 PRINT "VERTEX #","FACTOR #","COORDINATE"
220 FOR J=1 TO N+1
230 FOR I=1 TO N
```

```
240 PRINT J,I;
245 PRINT "                    ";
250 INPUT V1(J,I)
270 NEXT I
280 GOSUB 1000
290 R1(J)=R
300 NEXT J
302 PRINT
305 PRINT "SORT INITIAL VERTICES"
308 LET Y$="Y"
310 GOSUB 1500
320 GOSUB 9600
330 GOSUB 9800
340 C=1
350 GOSUB 3000
352 PRINT
354 PRINT "NEW VERTEX, NORMAL SIMPLEX"
355 FOR I=1 TO N
360 V2(I)=V(I)
362 PRINT V2(I);
365 NEXT I
410 GOSUB 2000
415 IF R=-100 THEN 5000
450 GOSUB 1000
460 R2=R
550 IF R2>R1(1) THEN 9000
560 IF R2>R1(N) THEN 8000
570 IF R2>R1(N+1) THEN 700
580 C=-0.5
590 GOSUB 3000
595 PRINT "NEW VERTEX, CW TYPE CONTRACTION"
600 FOR I=1 TO N
605 PRINT V(I);
```

```
610 V5(I)=V(I)
620 NEXT I
630 GOSUB 1000
640 R5=R
650 IF R5>R1(N+1) THEN 6000
660 PRINT "CW TYPE CONTRACTION FAILED"
670 PRINT "REJECT NEXT-TO-WORST VERTEX"
680 R1(N)=-100-D
690 GO TO 310
```

```
LIST 700,850
700 C=0.5
710 GOSUB 3000
715 PRINT "NEW VERTEX, CR TYPE CONTRACTION"
720 FOR I=1 TO N
730 V4(I)=V(I)
735 PRINT V(I);
740 NEXT I
750 GOSUB 1000
760 R4=R
770 IF R4>R2 THEN 7000
780 PRINT "CR TYPE CONTRACTION FAILED"
790 PRINT "REJECT NEXT-TO-WORST VERTEX"
810 R1(N)=-100-D
812 FOR I=1 TO N
814 V1(N+1,I)=V2(I)
816 NEXT I
818 R1(N+1)=R2
820 GO TO 310
```

```
LIST 1000,1300
1000 REM SUB FOR RESPONSES
1010 PRINT
1020 GOSUB 4500
1040 PRINT "RESPONSE BEING OPTIMIZED = ";K
1045 PRINT
1050 RETURN


LIST 1500,1700
1500 REM SUBROUTINE TO SORT & PRINT
1501 PRINT "******************************************************
1510 FOR K=1 TO N
1520 FOR Z=K+1 TO N+1
1530 IF R1(K)=>R1(Z) THEN 1620
1540 B=R1(K)
1550 R1(K)=R1(Z)
1560 R1(Z)=B
1570 FOR I=1 TO N
1580 B1=V1(K,I)
1590 V1(K,I)=V1(Z,I)
1600 V1(Z,I)=B1
1610 NEXT I
1620 NEXT Z
1630 NEXT K
1640 FOR J=1 TO N+1
1650 PRINT R1(J);
1660 FOR I=1 TO N
1670 PRINT V1(J,I);
1680 NEXT I
1685 PRINT
1690 NEXT J
1700 RETURN
```

```
LIST 2000,2200
2000 REM BOUND
2005 FOR I=1 TO N
2010 IF V(I)<L(I) THEN 2040
2020 IF V(I)>H(I) THEN 2040
2030 NEXT I
2035 GO TO 2050
2040 R=-100
2050 RETURN
```

```
LIST 3000,3300
3000 REM SUBROUTINE TO CALCULATE NEW VERTICES
3010 FOR I=1 TO N
3020 S=0
3030 FOR J=1 TO N
3080 S=S+V1(J,I)
3090 NEXT J
3100 P=S/N
3102 V(I)=P+C*(P-V1(N+1,I))
3110 NEXT I
3120 RETURN
```

```
LIST 4500,4700
4500 REM SUB TO CALCULATE RESPONSE
4510 R9=0
4511 W9=0
4520 FOR I=1 TO M
4530 PRINT " LINE   ";I;"   SIGNAL,BACKGROUND  ";
4540 INPUT S8(I),B8(I)
4550 IF S8(I)>B8(I) THEN 4570
4560 S8(I)=B8(I)+0.01
4570 R0(I)=(S8(I)-B8(I))/B8(I)
4580 PRINT "SIGNAL TO BACKGROUND RATIO =  ";R0(I)
4590 W8=(1/R0(I))↑W7
4600 R9=R9+R0(I)*W8
4610 W9=W9+W8
4620 NEXT I
4630 R=R9/W9
4635 PRINT
4640 RETURN
```

```
LIST 5000,5200
5000 REM BOUND VIOLATION NOR SIMP
5004 PRINT
5005 PRINT " BOUND VIOLATION IN NORMAL SIMPLEX "
5020 C=-0.5
5030 GOSUB 3000
5040 PRINT "NEW VERTEX CW CONTRACTION"
5050 FOR I=1 TO N
5060 PRINT V(I);
5070 V1(N+1,I)=V(I)
5075 NEXT I
5080 GOSUB 1000
5090 R1(N+1)=R
5100 GO TO 310

LIST 5500,5900
5500 REM BOUND VIOLATION ON ATTEMPTED EXPANSION
5502 PRINT
5503 R=-50
5505 PRINT " BOUND VIOLATION IN ATTEMPTED EXPANSION "
5510 GO TO 8000

LIST 6000,6200
6000 REM CW TYPE CONTRACTION
6001 PRINT "CW TYPE CONTRACTION SUCCESSFUL"
6005 R1(N+1)=R5
6010 FOR I=1 TO N
6020 V1(N+1,I)=V5(I)
6030 NEXT I
6032 IF R5>R1(N) THEN 6040
6034 R1(N)=-100-D
6040 GO TO 310
```

```
LIST 7000,7300
7000 REM CR TYPE CONTRACTION
7001 PRINT "CR TYPE CONTRACTION SUCCESSFUL"
7005 R1(N+1)=R4
7010 FOR I=1 TO N
7020 V1(N+1,I)=V4(I)
7030 NEXT I
7032 IF R4>R1(N) THEN 7040
7034 R1(N)=-100-D
7040 GO TO 310

LIST 8000,8400
8000 REM NORMAL SIMPLEX MOVE
8005 R1(N+1)=R2
8010 FOR I=1 TO N
8020 V1(N+1,I)=V2(I)
8030 NEXT I
8040 GO TO 310
```

```
LIST 9000,9500
9000 REM EXPAND
9010 C=2
9020 GOSUB 3000
9025 PRINT "NEW VERTEX,EXPANDED SIMPLEX"
9030 FOR I=1 TO N
9035 PRINT V(I);
9040 V3(I)=V(I)
9050 NEXT I
9060 GOSUB 2000
9070 IF R=-100 THEN 5500
9080 GOSUB 1000
9090 R3=R
9100 IF R3>R2 THEN 9300
9105 PRINT "ATTEMPTED EXPANSION FAILED"
9150 GO TO 8000
9300 REM SUCCESSFUL EXPANSION
9301 PRINT "SUCCESSFUL EXPANSION"
9310 R1(N+1)=R3
9320 FOR I=1 TO N
9330 V1(N+1,I)=V3(I)
9340 NEXT I
9350 GO TO 310
```

```
LIST 9600,9799
9600 REM VERTEX USED N+1 TIMES ?
9602 A1=0
9604 A2=0
9610 PRINT
9620 D=D+1
9630 PRINT "TIMES INTO MAIN LOOP = ";D
9640 PRINT
9650 W(D)=R1(1)
9651 FOR I=1 TO N
9652 W1(D,I)=V1(1,I)
9653 NEXT I
9656 FOR I=1 TO N+1
9657 A1=A1+R1(I)
9658 A2=A2+R1(I)↑2
9659 NEXT I
9660 A3=A2-A1↑2/(N+1)
9661 A4=SQR(A3/N)
9662 PRINT "STD DEV OF RESPONSE (LAST N+1 VERTICES) = ";A4
9663 PRINT
9665 IF D<N+1 THEN 9720
9667 IF W(D)=W(D-N) THEN 9671
9670 GO TO 9720
9671 FOR I=1 TO N
9673 IF W1(D,I)=W1(D-N,I) THEN 9678
9675 GO TO 9720
9678 NEXT I
9680 PRINT "VERTEX USED N+1 TIMES  --  RESPONSE WILL BE AVERAGED"
9690 GOSUB 1000
9700 R1(1)=(R1(1)+R)/2
9710 W(D)=R1(1)
9715 GOSUB 1500
9720 RETURN
```

```
LIST 9800,9999
9800 PRINT "TO CONTINUE TYPE Y";
9810 INPUT Y$
9820 IF Y$="Y" THEN 9840
9830 END
9840 RETURN
```

SEQUENTIAL SIMPLEX PROGRAM IN FORTRAN

```
C       J = VERTEX #
C       I = VARIABLE #
C       M = ELEMENT #
        REAL L
        INTEGER D,Z
        DIMENSION L(10), H(10), R1(10), V1(10,10)
        DIMENSION V(10), V2(10), V3(10), V4(10), V5(10)
        DIMENSION W(100), W1(100,6)
        DIMENSION S8(20), B8(20), R0(20)
C       THE FOLLOWING DATA SETS BOUNDS FOR N VARIABLES
C       AND INITIALIZES FIRST SIMPLEX
        DATA L(1)/700.0/
        DATA L(2)/7.0/
        DATA H(1)/1900.0/
        DATA H(2)/27.0/
        DATA V1(1,1)/800.0/
        DATA V1(2,1)/1250.0/
        DATA V1(3,1)/1700.0/
        DATA V1(1,2)/8.0/
        DATA V1(2,2)/25.0/
        DATA V1(3,2)/8.0/
        DATA M,N,W7/5,2,1.0/
        D = 0
        PRINT*, ' '
        PRINT*, ' THE NUMBER OF VARIABLES =',N
        PRINT*, ' THE NUMBER OF ELEMENTS =',  M
        PRINT*, ' POWER TO BE USED IN RESPNS FUNCTION =', W7
C       THE NEXT SET OF LOOPS PRINTS VERTICES OF FIRST SIMPLEX
        PRINT*, ' '
        PRINT*, ' INITIAL SIMPLEX'
```

```
      PRINT 10
10    FORMAT (1X,' VERTEX #',10X,'VARIABLE #',10X,'COORDINATE')
      DO 30 J = 1,N+1
      DO 20 I = 1,N
20    PRINT 25, J, I, V1(J,I)
25    FORMAT (4X,I2,16X,I2,18X,F7.2)
      CALL RESPNS (M,R,W7)
30    R1(J) = R
      PRINT*, ' '
      PRINT*, ' SORT INITIAL VERTICES'
35    CALL SORT (N,R1,V1)
      CALL AVG(D,N,R,R1,V1,W7,M)
      CALL CONTIN(YC)
      IF (YC.NE.'Y') GO TO 960
      C = 1.0
      CALL CALC (N,V1,C,V)
      PRINT*, ' '
      PRINT*, ' NEW VERTEX, NORMAL SIMPLEX'
      DO 40 I = 1,N
40    V2(I) = V(I)
      PRINT 50, (V(I),I = 1,N)
50    FORMAT (2X, 2(F10.5,5X))
      CALL BOUND (N,V,L,H,R)
      IF (R.EQ.-100.0) GO TO 400
      CALL RESPNS(M,R,W7)
      R2 = R
      IF (R2.GT.R1(1)) GO TO 900
      IF (R2.GT.R1(N)) GO TO 800
      IF (R2.GT.R1(N+1)) GO TO 65
      C = -0.5
      CALL CALC(N,V1,C,V)
      PRINT*, ' '
      PRINT*, ' NEW VERTEX, CW TYPE CONTRACTION'
      DO 60 I = 1,N
60    V5(I) = V(I)
```

```
      PRINT 50, (V(I), I = 1,N)
      CALL RESPNS (M,R,W7)
      R5 = R
      IF (R5.GT.R1(N+1)) GO TO 600
      PRINT*, ' '
      PRINT*, ' CW TYPE CONTRACTION FAILED'
      PRINT*, ' REJECT NEXT-TO-WORST VERTEX'
      R1(N) = -100.0-FLOAT(D)
      GO TO 35
65    PRINT 66
66    FORMAT (1X,' NEW VERTEX, CR TYPE CONTRACTION')
      C = 0.5
      CALL CALC (N,V1,C,V)
      DO 70 I = 1,N
70    V4(I) = V(I)
      PRINT 50, (V(I), I = 1,N)
      CALL RESPNS (M,R,W7)
      R4 = R
      IF (R4.GT.R2) GO TO 700
      PRINT*, ' '
      PRINT*, ' CR TYPE CONTRACTION FAILED'
      PRINT*, ' REJECT NEXT-TO-WORST VERTEX'
      R1(N) = -100.0-FLOAT(D)
      DO 75 I = 1,N
75    V1(N+1,I) = V2(I)
      R1(N+1) = R2
      GO TO 35
C     LOOP FOR BOUNDARY VIOLATION IN NORMAL SIMPLEX
400   PRINT 405
405   FORMAT (/,1X,' BOUNDARY VIOLATION IN NORMAL SIMPLEX')
      C = -0.5
      CALL CALC (N,V1,C,V)
      PRINT*, ' NEW VERTEX, CW CONTRACTION'
      DO 420 I = 1,N
420   V1(N+1,I) = V(I)
```

```
      PRINT 50, (V1(N+1,I), I = 1,N)
      CALL RESPNS (M,R,W7)
      R1(N+1) = R
      GO TO 35
C     LOOP FOR BOUNDARY VIOLATION IN ATTEMPTED EXPANSION
500   R = -50.0
      PRINT*, ' '
      PRINT*, ' BOUNDARY VIOLATION IN ATTEMPTED EXPANSION'
      GO TO 800
C     LOOP FOR CW TYPE CONTRACTION
600   PRINT 610
610   FORMAT (/, 1X,' CW TYPE CONTRACTION SUCCESSFUL')
      R1(N+1) = R5
      DO 620 I = 1,N
620   V1(N+1,I) = V5(I)
      IF (R5.LE.R1(N)) R1(N) = -100.0-FLOAT(D)
      GO TO 35
C     LOOP FOR CR TYPE CONTRACTION
700   PRINT 710
710   FORMAT (/, 1X,' CR TYPE CONTRACTION SUCCESSFUL')
      R1(N+1) = R4
      DO 720 I = 1,N
720   V1(N+1,I) = V4(I)
      IF (R4.LE.R1(N)) R1(N) = -100.0-FLOAT(D)
      GO TO 35
C     LOOP FOR NORMAL SIMPLEX MOVE
800   R1(N+1) = R2
      DO 810 I = 1,N
810   V1(N+1,I) = V2(I)
      GO TO 35
C     LOOP FOR SIMPLEX EXPANSION
900   PRINT 910
910   FORMAT (/' NEW VERTEX, EXPANDED SIMPLEX')
      C = 2.0
      CALL CALC (N,V1,C,V)
```

```
      DO 920 I = 1,N
920   V3(I) = V(I)
      PRINT 50, (V(I), I = 1,N)
      CALL BOUND (N,V,L,H,R)
      IF (R.EQ.-100.0) GO TO 500
      CALL RESPNS (M,R,W7)
      R3 = R
      IF (R3.GT.R2) GO TO 940
C     LOOP FOR FAILED EXPANSION
      PRINT*, ' ATTEMPTED EXPANSION FAILED'
      GO TO 800
C     LOOP FOR SUCCESSFUL EXPANSION
940   PRINT*, ' SUCCESSFUL EXPANSION'
      R1(N+1) = R3
      DO 950 I = 1,N
950   V1(N+1,I) = V3(I)
      GO TO 35
960   END
      SUBROUTINE RESPNS (M,R,W7)
C     SUBROUTINE TO CALCULATE RESPONSE
      DIMENSION RO(20),S8(20),B8(20)
      CALL WT (M,R,W7)
      PRINT 1000, R
1000  FORMAT (/, 1X,' RESPONSE BEING OPTIMIZED = ',F15.8)
      PRINT*, ' '
      RETURN
      END
      SUBROUTINE WT (M,R,W7)
C     SUBROUTINE TO CALC RESPONSE
      DIMENSION S8(20), B8(20), RO(20)
      R9 = 0
      W9 = 0
      PRINT*, ' '
      DO 1020 I = 1,M
      PRINT 1010, I
1010  FORMAT (1X, ' LINE ', I2, ' S,B ',5X, $)! INPUT PROMPT
```

```
      ACCEPT*, S8(I), B8(I)
      IF (S8(I).LE.B8(I)) S8(I) = B8(I) + 0.01
      RO(I) = (S8(I) - B8(I))/B8(I)
1020  PRINT 1025, RO(I)
1025  FORMAT (1X, ' S/B RATIO =', 5X,F12.8)
      DO 1030 I = 1,M
      W8 = (1/RO(I))**W7
      R9 = R9 + RO(I)*W8
1030  W9 = W9 + W8
      R = R9/W9
      RETURN
      END
      SUBROUTINE SORT (N,R1,V1)
C     SUBROUTINE TO SORT AND PRINT VERTICES
      DIMENSION R1(10), V1(10,10)
      INTEGER Z
      PRINT 100
100   FORMAT (//1X, 50('*'),/)
      DO 112 K = 1,N
      DO 111 Z = K+1,N+1
      IF (R1(K).GE.R1(Z)) GO TO 111
      B = R1(K)
      R1(K) = R1(Z)
      R1(Z) = B
      DO 110 I = 1,N
      B1 = V1(K,I)
      V1(K,I) = V1(Z,I)
      V1(Z,I) = B1
110   CONTINUE
111   CONTINUE
112   CONTINUE
      PRINT*, ' '
      DO 115, J = 1,N+1
115   PRINT 120, R1(J), (V1(J,I), I = 1,N)
120   FORMAT (1X, F15.5, 1X, 2(F7.2,1X))
```

```
      RETURN
      END
      SUBROUTINE BOUND (N,V,L,H,R)
C     SUBROUTINE TO CHECK FOR BOUNDARY VIOLATIONS
      REAL L
      DIMENSION V(10), L(10), H(10)
      DO 200 I = 1,N
      IF (V(I).LT.L(I)) GO TO 210
      IF (V(I).GT.H(I)) GO TO 210
200   CONTINUE
205   GO TO 220
210   R = -100.0
220   RETURN
      END
      SUBROUTINE CALC(N,V1,C,V)
C     SUBROUTINE TO CALCULATE NEW VERTICES
      DIMENSION V1(10,10), V(10)
      DO 310 I = 1,N
      SUM = 0.0
      DO 300 J = 1,N
      SUM = SUM + V1(J,I)
300   CONTINUE
      P = SUM/N
      V(I) = P + C*(P-V1(N+1,I))
310   CONTINUE
      RETURN
      END
      SUBROUTINE AVG(D,N,R,R1,V1,W7,M)
C     SUBROUTINE CHECKS WHETHER VERTEX USED N+1 TIMES
C     IF VERTEX USED N+1 TIMES, RESPONSES ARE AVERAGED
      DIMENSION R1(10), V1(10,10), W(100), W1(100,6)
      DIMENSION RO(20), S8(20), B8(20)
      INTEGER D
      A1 = 0
      A2 = 0
```

```
      PRINT*, ' '
      D = D+1
      PRINT*, ' TIMES INTO MAIN LOOP =',D
      PRINT*, ' '
      W(D) = R1(1)
      DO 960 I = 1,N
      W1(D,I) = V1(1,I)
960   CONTINUE
      DO 965 I = 1,N+1
      A1 = A1 + R1(I)
      A2 = A2 + R1(I)**2.0
965   CONTINUE
      A3 = A2 - A1**2.0/(N+1)
      A4 = SQRT(A3/N)
      PRINT 968, A4

968   FORMAT (1X,' STD DEV OF RESPONSE (LAST N+1 VERTICES) = ',F7.5)
      IF (D.LT.(N+1)) RETURN
      IF (W(D).NE.W(D-N)) RETURN
      DO 970 I = 1,N
      IF (W1(D,I).NE.W1(D-N,I)) RETURN
      IF (I.EQ.N) GO TO 980
970   CONTINUE
980   PRINT*, ' VERTEX USED N+1 TIMES---RESPONSES WILL BE AVERAGED'
      CALL RESPNS (M,R,W7)
      R1(1) = (R1(1) + R)/2.0
      W(D) = R1(1)
      CALL SORT (N,R1,V1)
      RETURN
      END
      SUBROUTINE CONTIN (YC)
C     SUBROUTINE ASKS IF USER WISHES TO CONTINUE
      PRINT 2000
2000  FORMAT (1X, ' TO CONTINUE TYPE Y ',$)! INPUT PROMPT
      ACCEPT 2010,YC
```

```
2010    FORMAT (A1)
        RETURN
        END
```

Appendix C

Printout of Experimental Data

Printout of Experimental Data

```
RUN
# OF DIMENSIONS = 2
# OF LINES = 5
POWER TO BE USED IN WEIGHTING FUNCTION -- RESPONSE SUB = 1

INITIAL SIMPLEX
VERTEX #             FACTOR #             COORDINATE
 1                    1                    800
 1                    2                    8

 LINE    1    SIGNAL,BACKGROUND    1589,491
SIGNAL TO BACKGROUND RATIO =  2.23625254582
 LINE    2    SIGNAL,BACKGROUND  1694,493
SIGNAL TO BACKGROUND RATIO =  2.43610547667
 LINE    3    SIGNAL,BACKGROUND  70.5,68
SIGNAL TO BACKGROUND RATIO =  0.0367647058824
 LINE    4    SIGNAL,BACKGROUND  1027.5,876
SIGNAL TO BACKGROUND RATIO =  0.172945205479
 LINE    5    SIGNAL,BACKGROUND  15,14
SIGNAL TO BACKGROUND RATIO =  0.0714285714286

RESPONSE BEING OPTIMIZED = 0.104515386259
```

```
 2                  1                  1250
 2                  2                  25

 LINE   1   SIGNAL,BACKGROUND  1583,192
SIGNAL TO BACKGROUND RATIO =  7.24479166667
 LINE   2   SIGNAL,BACKGROUND  444,122
SIGNAL TO BACKGROUND RATIO =  2.6393442623
 LINE   3   SIGNAL,BACKGROUND  49,28
SIGNAL TO BACKGROUND RATIO =  0.75
 LINE   4   SIGNAL,BACKGROUND  1515,3898
SIGNAL TO BACKGROUND RATIO =  2.565418162E-6
 LINE   5   SIGNAL,BACKGROUND  23,13
SIGNAL TO BACKGROUND RATIO =  0.769230769231

RESPONSE BEING OPTIMIZED = 1.282698715E-5

 3                  1                  16275,5140
 3                  2                  7310,2924

 LINE   1   SIGNAL,BACKGROUND
PROGRAM ABORTED IN LINE 4540
RUN 230
 3                  1                  1700
 3                  2                  8

 LINE   1   SIGNAL,BACKGROUND  16275,5140
SIGNAL TO BACKGROUND RATIO =  2.16634241245
 LINE   2   SIGNAL,BACKGROUND  7310,2924
SIGNAL TO BACKGROUND RATIO =  1.5
 LINE   3   SIGNAL,BACKGROUND  1019,992
SIGNAL TO BACKGROUND RATIO =  0.0272177419355
 LINE   4   SIGNAL,BACKGROUND  12322,9345
```

```
SIGNAL TO BACKGROUND RATIO =  0.318566078117
 LINE   5   SIGNAL,BACKGROUND  177.5,153
SIGNAL TO BACKGROUND RATIO =  0.160130718954

RESPONSE BEING OPTIMIZED = 0.105813434346


INVALID COMMAND ARGUMENT IN LINE 300 - MESSAGE NUMBER 19
 RUN 302

SORT INITIAL VERTICES
******************************************************
 0.105813434346 1700 8
 0.104515386259 800 8
 1.282698715E-5 1250 25


TIMES INTO MAIN LOOP = 1

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 0.0607127640901

TO CONTINUE TYPE YY

NEW VERTEX, NORMAL SIMPLEX
 1250 -9
 BOUND VIOLATION IN NORMAL SIMPLEX
NEW VERTEX CW CONTRACTION
 1250 16.5
 LINE   1   SIGNAL,BACKGROUND   6525.5,483
SIGNAL TO BACKGROUND RATIO =  12.5103519669
 LINE   2   SIGNAL,BACKGROUND  1659,453
SIGNAL TO BACKGROUND RATIO =  2.66225165563
 LINE   3   SIGNAL,BACKGROUND  147,96
SIGNAL TO BACKGROUND RATIO =  0.53125
```

```
 LINE   4   SIGNAL,BACKGROUND  1584,1341
SIGNAL TO BACKGROUND RATIO =  0.181208053691
 LINE   5   SIGNAL,BACKGROUND  45,15
SIGNAL TO BACKGROUND RATIO =  2

RESPONSE BEING OPTIMIZED = 0.598341840211

*******************************************************
 0.598341840211 1250 16.5
 0.105813434346 1700 8
 0.104515386259 800 8

TIMES INTO MAIN LOOP = 2

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 0.284736861603

TO CONTINUE TYPE YY

NEW VERTEX, NORMAL SIMPLEX
 2150 16.5
 BOUND VIOLATION IN NORMAL SIMPLEX
NEW VERTEX CW CONTRACTION
 1137.5 10.125
 LINE   1   SIGNAL,BACKGROUND   10031,1205
SIGNAL TO BACKGROUND RATIO =  7.3244813278
 LINE   2   SIGNAL,BACKGROUND  5315.5,1413
SIGNAL TO BACKGROUND RATIO =  2.7618542109
 LINE   3   SIGNAL,BACKGROUND  186,170
SIGNAL TO BACKGROUND RATIO =  0.0941176470588
 LINE   4   SIGNAL,BACKGROUND  2547,1900
SIGNAL TO BACKGROUND RATIO =  0.340526315789
 LINE   5   SIGNAL,BACKGROUND  40,29
SIGNAL TO BACKGROUND RATIO =  0.379310344828
```

```
RESPONSE BEING OPTIMIZED = 0.299462196971

**********************************************************
 0.598341840211 1250 16.5
 0.299462196971 1137.5 10.125
 0.105813434346 1700 8

TIMES INTO MAIN LOOP = 3

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 0.248130716556

TO CONTINUE TYPE YY

NEW VERTEX, NORMAL SIMPLEX
 687.5 18.625
 BOUND VIOLATION IN NORMAL SIMPLEX
NEW VERTEX CW CONTRACTION
 1446.875 10.65625


 LINE   1   SIGNAL,BACKGROUND
12711,2133
SIGNAL TO BACKGROUND RATIO =  4.95921237693
 LINE   2   SIGNAL,BACKGROUND  5053.5,1652
SIGNAL TO BACKGROUND RATIO =  2.05901937046
 LINE   3   SIGNAL,BACKGROUND  449.5,396
SIGNAL TO BACKGROUND RATIO =  0.135101010101
 LINE   4   SIGNAL,BACKGROUND  4986.5,3765
SIGNAL TO BACKGROUND RATIO =  0.324435590969
 LINE   5   SIGNAL,BACKGROUND  92.5,61
SIGNAL TO BACKGROUND RATIO =  0.516393442623

RESPONSE BEING OPTIMIZED = 0.381447434427
```

```
*******************************************************
 0.598341840211 1250 16.5
 0.381447434427 1446.875 10.65625
 0.299462196971 1137.5 10.125

TIMES INTO MAIN LOOP = 4

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 0.154431108462

VERTEX USED N+1 TIMES  --  RESPONSE WILL BE AVERAGED

 LINE   1   SIGNAL,BACKGROUND   7036.5,512
SIGNAL TO BACKGROUND RATIO =  12.7431640625
 LINE   2   SIGNAL,BACKGROUND  1813,522
SIGNAL TO BACKGROUND RATIO =  2.47318007663
 LINE   3   SIGNAL,BACKGROUND  151,97
SIGNAL TO BACKGROUND RATIO =  0.556701030928
 LINE   4   SIGNAL,BACKGROUND  1704.5,1378
SIGNAL TO BACKGROUND RATIO =  0.236937590711
 LINE   5   SIGNAL,BACKGROUND  47,17
SIGNAL TO BACKGROUND RATIO =  1.76470588235


RESPONSE BEING OPTIMIZED = 0.7075844042

*******************************************************
 0.652963122205 1250 16.5
 0.381447434427 1446.875 10.65625
 0.299462196971 1137.5 10.125
TO CONTINUE TYPE YY

NEW VERTEX, NORMAL SIMPLEX
 1559.375 17.03125
```

```
 LINE   1   SIGNAL,BACKGROUND   7307,933
SIGNAL TO BACKGROUND RATIO =  6.83172561629
 LINE   2   SIGNAL,BACKGROUND  1508,585
SIGNAL TO BACKGROUND RATIO =  1.57777777778
 LINE   3   SIGNAL,BACKGROUND  280,198
SIGNAL TO BACKGROUND RATIO =  0.414141414141
 LINE   4   SIGNAL,BACKGROUND  3569,3890
SIGNAL TO BACKGROUND RATIO =  2.570694086E-6
 LINE   5   SIGNAL,BACKGROUND  89.5,34
SIGNAL TO BACKGROUND RATIO =  1.63235294118

RESPONSE BEING OPTIMIZED = 1.285334463E-5

NEW VERTEX, CW TYPE CONTRACTION
 1242.96875 11.8515625
 LINE   1   SIGNAL,BACKGROUND   10634,1180
SIGNAL TO BACKGROUND RATIO =  8.01186440678
 LINE   2   SIGNAL,BACKGROUND  4399.5,1245
SIGNAL TO BACKGROUND RATIO =  2.53373493976
 LINE   3   SIGNAL,BACKGROUND  244.5,204
SIGNAL TO BACKGROUND RATIO =  0.198529411765
 LINE   4   SIGNAL,BACKGROUND  4183,2143
SIGNAL TO BACKGROUND RATIO =  0.951936537564
 LINE   5   SIGNAL,BACKGROUND  56.5,33
SIGNAL TO BACKGROUND RATIO =  0.712121212121

RESPONSE BEING OPTIMIZED = 0.624120635847

CW TYPE CONTRACTION SUCCESSFUL
******************************************************
 0.652963122205 1250 16.5
 0.624120635847 1242.96875 11.8515625
 0.381447434427 1446.875 10.65625
```

```
TIMES INTO MAIN LOOP = 5

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 0.149132458135

TO CONTINUE TYPE YY

NEW VERTEX, NORMAL SIMPLEX
 1046.09375 17.6953125
 LINE   1   SIGNAL,BACKGROUND   4917,269
SIGNAL TO BACKGROUND RATIO =  17.2788104089
 LINE   2   SIGNAL,BACKGROUND  1617,419
SIGNAL TO BACKGROUND RATIO =  2.85918854415
 LINE   3   SIGNAL,BACKGROUND  68.5,40
SIGNAL TO BACKGROUND RATIO =  0.7125
 LINE   4   SIGNAL,BACKGROUND  876.5,770
SIGNAL TO BACKGROUND RATIO =  0.138311688312
 LINE   5   SIGNAL,BACKGROUND  22,9
SIGNAL TO BACKGROUND RATIO =  1.44444444444

RESPONSE BEING OPTIMIZED = 0.513690501699

NEW VERTEX, CR TYPE CONTRACTION
 1146.2890625 15.935546875
 LINE   1   SIGNAL,BACKGROUND    6651.5,438
SIGNAL TO BACKGROUND RATIO =  14.1860730594
 LINE   2   SIGNAL,BACKGROUND  2036,531
SIGNAL TO BACKGROUND RATIO =  2.83427495292
 LINE   3   SIGNAL,BACKGROUND  118.5,79
SIGNAL TO BACKGROUND RATIO =  0.5
 LINE   4   SIGNAL,BACKGROUND  1300,1007
SIGNAL TO BACKGROUND RATIO =  0.2909632572
 LINE   5   SIGNAL,BACKGROUND  35,14
SIGNAL TO BACKGROUND RATIO =  1.5
```

```
RESPONSE BEING OPTIMIZED = 0.766067226668

CR TYPE CONTRACTION SUCCESSFUL
*****************************************************
 0.766067226668 1146.2890625 15.935546875
 0.652963122205 1250 16.5
 0.624120635847 1242.96875 11.8515625

TIMES INTO MAIN LOOP = 6

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 0.0750258423383

TO CONTINUE TYPE YY

NEW VERTEX, NORMAL SIMPLEX
 1153.3203125 20.583984375
 LINE   1   SIGNAL,BACKGROUND   3868,241
SIGNAL TO BACKGROUND RATIO =  15.0497925311
 LINE   2   SIGNAL,BACKGROUND  985,256
SIGNAL TO BACKGROUND RATIO =  2.84765625
 LINE   3   SIGNAL,BACKGROUND  70.5,40
SIGNAL TO BACKGROUND RATIO =  0.7625
 LINE   4   SIGNAL,BACKGROUND  1029.5,1684
SIGNAL TO BACKGROUND RATIO =  5.938242277E-6
 LINE   5   SIGNAL,BACKGROUND  25,10
SIGNAL TO BACKGROUND RATIO =  1.5

RESPONSE BEING OPTIMIZED = 2.969078899E-5

NEW VERTEX, CW TYPE CONTRACTION
 1220.55664063 14.0346679688
 LINE   1   SIGNAL,BACKGROUND   8177.5,655
SIGNAL TO BACKGROUND RATIO =  11.4847328244
```

```
 LINE   2   SIGNAL,BACKGROUND  2857.5,789
SIGNAL TO BACKGROUND RATIO =  2.6216730038
 LINE   3   SIGNAL,BACKGROUND  163,116
SIGNAL TO BACKGROUND RATIO =  0.405172413793
 LINE   4   SIGNAL,BACKGROUND  1850,1233
SIGNAL TO BACKGROUND RATIO =  0.500405515004
 LINE   5   SIGNAL,BACKGROUND  44,19
SIGNAL TO BACKGROUND RATIO =  1.31578947368

RESPONSE BEING OPTIMIZED = 0.877967395772

CW TYPE CONTRACTION SUCCESSFUL
*****************************************************
 0.877967395772 1220.55664063 14.0346679688
 0.766067226668 1146.2890625 15.935546875
 0.652963122205 1250 16.5

TIMES INTO MAIN LOOP = 7

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 0.112502673609

TO CONTINUE TYPE YY

NEW VERTEX, NORMAL SIMPLEX
 1116.84570313 13.4702148438

 LINE   1   SIGNAL,BACKGROUND  8102.5,616
SIGNAL TO BACKGROUND RATIO =  12.1534090909
 LINE   2   SIGNAL,BACKGROUND  3246.5,872
SIGNAL TO BACKGROUND RATIO =  2.72305045872
 LINE   3   SIGNAL,BACKGROUND  129,95
SIGNAL TO BACKGROUND RATIO =  0.357894736842
 LINE   4   SIGNAL,BACKGROUND  1622,1122
SIGNAL TO BACKGROUND RATIO =  0.445632798574
```

```
 LINE   5   SIGNAL,BACKGROUND  33.5,17
SIGNAL TO BACKGROUND RATIO =  0.970588235294

RESPONSE BEING OPTIMIZED = 0.767113850735

******************************************************
 0.877967395772 1220.55664063 14.0346679688
 0.767113850735 1116.84570313 13.4702148438
 0.766067226668 1146.2890625 15.935546875

TIMES INTO MAIN LOOP = 8

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 0.0643095877753

TO CONTINUE TYPE YY

NEW VERTEX, NORMAL SIMPLEX
 1191.11328125 11.5693359375
 LINE   1   SIGNAL,BACKGROUND   10553,1071
SIGNAL TO BACKGROUND RATIO =  8.85340802988
 LINE   2   SIGNAL,BACKGROUND  4723.5,1232
SIGNAL TO BACKGROUND RATIO =  2.83400974026
 LINE   3   SIGNAL,BACKGROUND  202,172
SIGNAL TO BACKGROUND RATIO =  0.174418604651
 LINE   4   SIGNAL,BACKGROUND  2653,1791
SIGNAL TO BACKGROUND RATIO =  0.481295365717
 LINE   5   SIGNAL,BACKGROUND  46.5,29
SIGNAL TO BACKGROUND RATIO =  0.603448275862

RESPONSE BEING OPTIMIZED = 0.503321407848

NEW VERTEX, CW TYPE CONTRACTION
 1157.49511719 14.8439941406
 LINE   1   SIGNAL,BACKGROUND   7569.5539
```

```
539
SIGNAL TO BACKGROUND RATIO =  13.0436992579
 LINE   2   SIGNAL,BACKGROUND  2604.5,680
SIGNAL TO BACKGROUND RATIO =  2.83014705882
 LINE   3   SIGNAL,BACKGROUND  136,93
SIGNAL TO BACKGROUND RATIO =  0.462365591398
 LINE   4   SIGNAL,BACKGROUND  1550,1137
SIGNAL TO BACKGROUND RATIO =  0.363236587511
 LINE   5   SIGNAL,BACKGROUND  37.5,16
SIGNAL TO BACKGROUND RATIO =  1.34375

RESPONSE BEING OPTIMIZED = 0.821017081521

CW TYPE CONTRACTION SUCCESSFUL
*****************************************************
 0.877967395772 1220.55664063 14.0346679688
 0.821017081521 1157.49511719 14.8439941406
 0.767113850735 1116.84570313 13.4702148438

TIMES INTO MAIN LOOP = 9

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 0.055433751797

VERTEX USED N+1 TIMES  --  RESPONSE WILL BE AVERAGED

 LINE   1   SIGNAL,BACKGROUND   8753.5,671
SIGNAL TO BACKGROUND RATIO =  12.0454545455
 LINE   2   SIGNAL,BACKGROUND  3106.5,800
SIGNAL TO BACKGROUND RATIO =  2.883125
 LINE   3   SIGNAL,BACKGROUND  167,119
SIGNAL TO BACKGROUND RATIO =  0.403361344538
 LINE   4   SIGNAL,BACKGROUND  1939.5,1274
SIGNAL TO BACKGROUND RATIO =  0.522370486656
```

```
 LINE   5   SIGNAL,BACKGROUND  45,20
SIGNAL TO BACKGROUND RATIO =  1.25

RESPONSE BEING OPTIMIZED = 0.889144722673

******************************************************
 0.883556059223 1220.55664063 14.0346679688
 0.821017081521 1157.49511719 14.8439941406
 0.767113850735 1116.84570313 13.4702148438
TO CONTINUE TYPE YY

NEW VERTEX, NORMAL SIMPLEX
 1261.20605469 15.4084472656
 LINE   1   SIGNAL,BACKGROUND   7631.5,595
SIGNAL TO BACKGROUND RATIO =  11.8260504202
 LINE   2   SIGNAL,BACKGROUND  2181.5,606
SIGNAL TO BACKGROUND RATIO =  2.5998349835
 LINE   3   SIGNAL,BACKGROUND  168.5,114
SIGNAL TO BACKGROUND RATIO =  0.478070175439
 LINE   4   SIGNAL,BACKGROUND  1819,1403
SIGNAL TO BACKGROUND RATIO =  0.296507483963
 LINE   5   SIGNAL,BACKGROUND  49.5,19
SIGNAL TO BACKGROUND RATIO =  1.60526315789

RESPONSE BEING OPTIMIZED = 0.762603280428

NEW VERTEX, CW TYPE CONTRACTION
 1152.93579102 13.9547729492
 LINE   1   SIGNAL,BACKGROUND   8255.5,617
SIGNAL TO BACKGROUND RATIO =  12.3800648298
 LINE   2   SIGNAL,BACKGROUND  3043.5,802
SIGNAL TO BACKGROUND RATIO =  2.79488778055
```

```
 LINE   3   SIGNAL,BACKGROUND  142.[redacted],103
SIGNAL TO BACKGROUND RATIO =  0.383495145631
 LINE   4   SIGNAL,BACKGROUND  1704.5,1213
SIGNAL TO BACKGROUND RATIO =  0.405193734542
 LINE   5   SIGNAL,BACKGROUND  38.5,18
SIGNAL TO BACKGROUND RATIO =  1.13888888889

RESPONSE BEING OPTIMIZED = 0.782206969581

CW TYPE CONTRACTION SUCCESSFUL
*****************************************************
 0.883556059223 1220.55664063 14.0346679688
 0.782206969581 1152.93579102 13.9547729492
 -109 1157.49511719 14.8439941406

TIMES INTO MAIN LOOP = 10

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 63.412063956

TO CONTINUE TYPE YY

NEW VERTEX, NORMAL SIMPLEX
 1215.99731445 13.1454467773
 LINE   1   SIGNAL,BACKGROUND   9202.5,801
SIGNAL TO BACKGROUND RATIO =  10.4887640449
 LINE   2   SIGNAL,BACKGROUND  3524.5,947
SIGNAL TO BACKGROUND RATIO =  2.72175290391
 LINE   3   SIGNAL,BACKGROUND  182.5,138
SIGNAL TO BACKGROUND RATIO =  0.322463768116
 LINE   4   SIGNAL,BACKGROUND  2150,1478
SIGNAL TO BACKGROUND RATIO =  0.454668470907
 LINE   5   SIGNAL,BACKGROUND  47,23
SIGNAL TO BACKGROUND RATIO =  1.04347826087
```

```
RESPONSE BEING OPTIMIZED = 0.743869169056

NEW VERTEX, CR TYPE CONTRACTION
 1201.37176514 13.5700836182
 LINE   1   SIGNAL,BACKGROUND   8705.5,691
SIGNAL TO BACKGROUND RATIO =  11.5984081042
 LINE   2   SIGNAL,BACKGROUND  3258,842
SIGNAL TO BACKGROUND RATIO =  2.86935866983
 LINE   3   SIGNAL,BACKGROUND  159.5,117
SIGNAL TO BACKGROUND RATIO =  0.363247863248
 LINE   4   SIGNAL,BACKGROUND  1890,1317
SIGNAL TO BACKGROUND RATIO =  0.435079726651
 LINE   5   SIGNAL,BACKGROUND  42.5,20
SIGNAL TO BACKGROUND RATIO =  1.125

RESPONSE BEING OPTIMIZED = 0.784315196058

CR TYPE CONTRACTION SUCCESSFUL
*****************************************************
 0.883556059223 1220.55664063 14.0346679688
 0.784315196058 1201.37176514 13.5700836182
 0.782206969581 1152.93579102 13.9547729492

TIMES INTO MAIN LOOP = 11

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 0.0579149254101

VERTEX USED N+1 TIMES  --  RESPONSE WILL BE AVERAGED

 LINE   1   SIGNAL,BACKGROUND   8603.5,731
SIGNAL TO BACKGROUND RATIO =  10.7694938441
 LINE   2   SIGNAL,BACKGROUND  2884,861
SIGNAL TO BACKGROUND RATIO =  2.34959349594
```

```
LINE   3   SIGNAL,BACKGROUND  180,129
SIGNAL TO BACKGROUND RATIO =  0.395348837209
 LINE   4   SIGNAL,BACKGROUND  2101,1457
SIGNAL TO BACKGROUND RATIO =  0.442004118051
 LINE   5   SIGNAL,BACKGROUND  48,21
SIGNAL TO BACKGROUND RATIO =  1.28571428571

RESPONSE BEING OPTIMIZED = 0.821278024048

*******************************************************
 0.852417041635 1220.55664063 14.0346679688
 0.784315196058 1201.37176514 13.5700836182
 0.782206969581 1152.93579102 13.9547729492
TO CONTINUE TYPE YY

NEW VERTEX, NORMAL SIMPLEX
 1268.99261475 13.6499786377
 LINE   1   SIGNAL,BACKGROUND   9527,856
SIGNAL TO BACKGROUND RATIO =  10.1296728972
 LINE   2   SIGNAL,BACKGROUND  3352,924
SIGNAL TO BACKGROUND RATIO =  2.62770562771
 LINE   3   SIGNAL,BACKGROUND  207,155
SIGNAL TO BACKGROUND RATIO =  0.335483870968
 LINE   4   SIGNAL,BACKGROUND  2374.5,1653
SIGNAL TO BACKGROUND RATIO =  0.436479128857
 LINE   5   SIGNAL,BACKGROUND  54.5,25
SIGNAL TO BACKGROUND RATIO =  1.18

RESPONSE BEING OPTIMIZED = 0.757740261657

NEW VERTEX, CW TYPE CONTRACTION
 1181.94999695 13.8785743713
 LINE   1   SIGNAL,BACKGROUND   8616.5,661
SIGNAL TO BACKGROUND RATIO =  12.0355521936
```

```
 LINE   2   SIGNAL,BACKGROUND  3213.5,805
SIGNAL TO BACKGROUND RATIO =  2.99192546584
 LINE   3   SIGNAL,BACKGROUND  154.5,113
SIGNAL TO BACKGROUND RATIO =  0.367256637168
 LINE   4   SIGNAL,BACKGROUND  1831,1283
SIGNAL TO BACKGROUND RATIO =  0.427123928293
 LINE   5   SIGNAL,BACKGROUND  41,19
SIGNAL TO BACKGROUND RATIO =  1.15789473684

RESPONSE BEING OPTIMIZED = 0.788011023364

CW TYPE CONTRACTION SUCCESSFUL
**************************************************
 0.852417041635 1220.55664063 14.0346679688
 0.788011023364 1181.94999695 13.8785743713
 0.784315196058 1201.37176514 13.5700836182

TIMES INTO MAIN LOOP = 12

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 0.0382963351165

TO CONTINUE TYPE YY

NEW VERTEX, NORMAL SIMPLEX
 1201.13487244 14.3431587219
 LINE   1   SIGNAL,BACKGROUND   8291.5,634
SIGNAL TO BACKGROUND RATIO =  12.0780757098
 LINE   2   SIGNAL,BACKGROUND  2897,782
SIGNAL TO BACKGROUND RATIO =  2.70460358056
 LINE   3   SIGNAL,BACKGROUND  155.5,109
SIGNAL TO BACKGROUND RATIO =  0.426605504587
 LINE   4   SIGNAL,BACKGROUND  1831,1279
SIGNAL TO BACKGROUND RATIO =  0.431587177482
```

```
 LINE   5   SIGNAL,BACKGROUND  43,18
SIGNAL TO BACKGROUND RATIO =  1.38888888889

RESPONSE BEING OPTIMIZED = 0.857096387017


NEW VERTEX,EXPANDED SIMPLEX
 1201.01642609 14.7296962738
 LINE   1   SIGNAL,BACKGROUND   8141,607
SIGNAL TO BACKGROUND RATIO =  12.4118616145
 LINE   2   SIGNAL,BACKGROUND  2780.5,725
SIGNAL TO BACKGROUND RATIO =  2.83517241379
 LINE   3   SIGNAL,BACKGROUND  153,107
SIGNAL TO BACKGROUND RATIO =  0.429906542056
 LINE   4   SIGNAL,BACKGROUND  1789.5,1304
SIGNAL TO BACKGROUND RATIO =  0.37231595092
 LINE   5   SIGNAL,BACKGROUND  43,18
SIGNAL TO BACKGROUND RATIO =  1.38888888889

RESPONSE BEING OPTIMIZED = 0.810996053159

ATTEMPTED EXPANSION FAILED
*****************************************************
 0.857096387017 1201.13487244 14.3431587219
 0.852417041635 1220.55664063 14.0346679688
 0.788011023364 1181.94999695 13.8785743713

TIMES INTO MAIN LOOP = 13

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 0.038606603351

TO CONTINUE TYPE YY
```

```
NEW VERTEX, NORMAL SIMPLEX
 1239.74151611 14.4992523193
 LINE   1   SIGNAL,BACKGROUND   8328,653
SIGNAL TO BACKGROUND RATIO =  11.7534456355
 LINE   2   SIGNAL,BACKGROUND  2714.5,732
SIGNAL TO BACKGROUND RATIO =  2.70833333333
 LINE   3   SIGNAL,BACKGROUND  170,120
SIGNAL TO BACKGROUND RATIO =  0.416666666667
 LINE   4   SIGNAL,BACKGROUND  1940,1407
SIGNAL TO BACKGROUND RATIO =  0.37882018479
 LINE   5   SIGNAL,BACKGROUND  47,20
SIGNAL TO BACKGROUND RATIO =  1.35

RESPONSE BEING OPTIMIZED = 0.80194676716

NEW VERTEX, CR TYPE CONTRACTION
 1225.29363632 14.3440828323
 LINE   1   SIGNAL,BACKGROUND   8362.5,654
SIGNAL TO BACKGROUND RATIO =  11.7866972477
 LINE   2   SIGNAL,BACKGROUND  2686.5,734
SIGNAL TO BACKGROUND RATIO =  2.66008174387
 LINE   3   SIGNAL,BACKGROUND  172.5,119
SIGNAL TO BACKGROUND RATIO =  0.449579831933
 LINE   4   SIGNAL,BACKGROUND  1982,1319
SIGNAL TO BACKGROUND RATIO =  0.502653525398
 LINE   5   SIGNAL,BACKGROUND  48,20
SIGNAL TO BACKGROUND RATIO =  1.4

RESPONSE BEING OPTIMIZED = 0.927850973356
```

```
CR TYPE CONTRACTION SUCCESSFUL
******************************************************
 0.927850973356 1225.29363632 14.3440828323
 0.857096387017 1201.13487244 14.3431587219
 0.852417041635 1220.55664063 14.0346679688

TIMES INTO MAIN LOOP = 14

STD DEV OF RESPONSE (LAST N+1 VERTICES) = 0.0422657974724

TO CONTINUE TYPE YY
```