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# Comparison of Alternating Variable Search and Simplex Methods of Optimisation for Inductively Coupled Plasma Optical Emission and Atomic Fluorescence Spectrometry

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The performance of several cyclic alternating variable search (AVS) optimisation methods are compared with two simplex methods with respect to the number of changes of variable required to search a model two-factor response space. The roles of the initial step size and of the variable step size are discussed, and the information produced concerning the shape of the factor space is evaluated. An AVS method which starts with a fixed step size and then changes to a variable step size on second and subsequent cycles is compared with a variable step size simplex for the optimisation of an inductively coupled plasma optical emission spectrometer and of the atomiser, source inductively coupled plasmas in atomic fluorescence spectrometry (the ASIA system). The order in which the variables are taken in the AVS method does not affect the value of the optimum eventually found. Both methods perform satisfactorily for the optical emission work, although the AVS method provides information about the shape of the factor space which is easier to interpret than in the simplex method. However, the simplex method was not always able to satisfy the conditions for termination in the case of the atomic fluorescence studies and was much slower to implement than the AVS method as the latter used direct visual feedback from the output of the lock-in amplifier as a measure of the figure of merit (total fluorescence signal).

**Keywords:** *Inductively coupled plasma optical emission spectrometry; inductively coupled plasma atomic fluorescence spectrometry; atomiser, source inductively coupled plasmas in atomic fluorescence spectrometry; simplex method; alternating variable search optimisation*

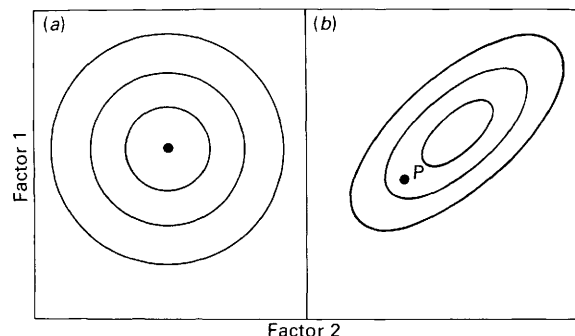
Optimisation may be considered as the process by which a maximum (or minimum) in a factor space is located. What is required is an efficient strategy for locating the maximum value on an  $n + 1$  dimensional response surface, where  $n$  is the number of factors contributing to the response. The efficiency of optimisation is normally quantified in terms of the time taken to locate the maximum. This has an effect on the mechanism of the search strategy in terms of selection of (a) the step size and (b) the criterion for stopping.

There are several optimisation methods described in the literature of which the alternating variable search (AVS) (sometimes referred to as the iterative univariate method), steepest ascent and simplex methods are probably the most widely used in analytical chemistry. Each of these methods has a number of variants. It is common practice in modern texts dealing with optimisation strategies to refer to the AVS method as the "classical," "intuitive" or "traditional" method.<sup>1,2</sup> More recent methods, which involve computation, are generally referred to as chemometric techniques.<sup>3</sup> Factorial design methods,<sup>1</sup> although intended to give information about the effects of factors on the response and about the interaction among factors, may also function as a strategy for locating the maximum in the response surface. However, some prior knowledge of the nature of the response surface is needed and the method can fail if the model used or the coding (usually a logarithmic transformation) of the variables is inadequate.<sup>3</sup>

To illustrate the steepest ascent and simplex methods, diagrams such as those shown in Fig. 1 are often used. These represent the situation for two factors with the 3-dimensional response surface represented by contour plots. The response surface shown in Fig. 1(a) illustrates a situation in which the two factors are independent. Whichever method was chosen to search this factor space, would locate the maximum as closely as the chosen step size allowed. If the criterion for stopping is that a decreased response is obtained in whatever direction, a step is taken, then a large step size means that the

search may stop some distance from the position of the maximum as it would be possible for the search to "step over" an intervening higher value. Differences in the methods are apparent when the situation shown in Fig. 1(b) is encountered and this situation is usually chosen to illustrate the failure of AVS methods. The reason for this failure is that if the AVS search locates a point,  $P$ , on the ridge, then as the search directions can only be parallel to the axes, the criterion for location of a maximum will be satisfied. When the step size is large compared with the distance across the contours in all four search directions, the response decreases and the point,  $P$ , is erroneously concluded to represent the optimum. This apparently severe limitation of AVS methods will be examined more closely later. The AVS methods are also criticised on the basis that the optimum found depends on the starting position for the search, and the order in which the factors are taken. The number of steps necessary to find the optimum is also given as a drawback of AVS methods.<sup>4,5</sup>

Until such time as all manufacturers of chemical instrumentation supply the necessary computing power and software to run a multivariate chemometric optimisation method (the composite modified simplex method of Betteridge *et al.*<sup>4</sup> would seem to be a good choice), users of plasma spectrometers are faced with a choice. Either purchase a computer



**Fig. 1.** Hypothetical contour plots of response surfaces for two factors, (a) independent factors (circular contours) and (b) dependent factors (ellipsoidal contours)

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(and software) to stand alongside the instrument or use a method which requires no computation (other than that of the desired response function). A possible third option is the manual calculation of a multivariate chemometric method: the use of this procedure has been reported<sup>6,7</sup> in connection with plasma spectrometry involving three variables (injector flow-rate, power and observation height) and was described as "rapid and effective." Effective though the method may be, it is not considered to be viable in this present situation because manual calculations are time consuming and tedious.

There are situations in which the time required for the optimisation is of secondary importance compared with the accuracy of location of the optimum conditions. Many research studies concerned with gaining a clearer understanding of the underlying physical and/or chemical processes of the system under study will adopt the strategy of locating an optimum and then studying the change in response as a function of factor level as each factor is varied in turn, while holding the others constant. Valid comparisons of different systems can only be made if the maximum in the same response surface has been located for each system before any comparisons are made. Many studies of this nature have a timescale of months or years.

The aim of this study was to compare the performance of AVS and simplex methods in three situations; firstly to locate the maximum of a model response surface, secondly to operate routinely a plasma spectrometer for atomic emission spectrometry and thirdly to operate routinely a dual plasma atomic fluorescence spectrometer. The first situation is based on a previously described model response surface<sup>2</sup> and for the second it is known that both the AVS<sup>8</sup> and simplex<sup>6</sup> are capable of locating a maximum in the signal to background ratio (SBR) response surface.

## Experimental

### Alternating Variable Search Methods

Several variations of the AVS methods were used, all of which involved initial decisions concerning the boundaries or limits of the factor space and of the initial step size for each factor. Step sizes were chosen to be between 0.1 and 0.05 of the appropriate factor space. As a rough guide for the choice of step size, the criterion that two steps from the starting position should cause a significant difference in the response value was used. For all methods the standard deviation of the response was estimated after the first successful cycle by replicate measurement. The search was terminated when the responses obtained at the end of two successive cycles were within two standard deviations.

#### Fixed step size method

Two methods were used which differed only in the rule for changing direction. In the first (fixed AVS-1) the search changed direction after one step in a bad direction (*i.e.*, a decrease in response) whereas in the second (fixed AVS-2) a change of direction was made after two successive bad steps had been taken.

#### Rosenbrock's method

This is a variable step size method<sup>9</sup> in which the step size was increased by a factor of three if the search was proceeding in a good direction. If the search direction was bad a contracted step of half the previous step size was taken and then the search direction was changed.

#### Hybrid method

In this method the first cycle of the factors (*i.e.*, all factors taken in turn) proceeded with a fixed step size. For subsequent

cycles the initial step size was increased by a factor of three if the search was proceeding in a good direction. As long as the response increased, the initial step size was repeated followed by a "triple jump." If the factor of three expansion gave a bad response, a step (of initial size) was taken in the reverse direction (equivalent to a replacement step of factor two expansion). The direction was then changed. When a bad response was obtained for the initial step size following a triple jump a further unit step was taken. If two successive bad steps had then been taken, the search direction was changed, otherwise a triple jump was taken. The flow diagram of this hybrid method is shown in Fig. 2.

#### Simplex method

Software was used to implement the method described previously<sup>6</sup> on an Apple IIe computer. This is a variable step size simplex based on the modification of Nelder and Mead<sup>10</sup> to the procedure set out by Spendley *et al.*<sup>11</sup> The initial simplex and step size are calculated according to the method of Yarbrow and Deming.<sup>12</sup> The simplex method terminates when the responses at all the vertices of the current simplex are within an operator-determined relative standard deviation, which may not be possible if the system is very noisy. The optimum conditions are those of the vertex giving the highest signal to background ratio (SBR) in the final simplex.

#### Instrumentation

The instrument used for this work, known as ASIA (atomiser, source inductively coupled plasmas in atomic fluorescence spectrometry) has been described in detail elsewhere.<sup>13</sup> It is both an atomic fluorescence and atomic emission spectrometer. In the emission mode, the plasma is sustained in a Scott- or Fassel-type torch used with a Meinhard nebuliser and Scott spray chamber. In the fluorescence mode, an extended-sleeve Baird torch is used. The output signal from the lock-in amplifier was processed by an Apple IIe computer.

A short program was written to facilitate rapid data collection and automatic calculation of the SBR. The same program was used to collect data in both the AVS and simplex experiments. Although not absolutely necessary for the AVS method the computer was used to allow direct comparison of the two methods. Signals were integrated for a period of 10 s. For the emission studies the SBR was taken as the figure of merit<sup>14</sup> to be maximised. For the fluorescence studies the figure of merit used was total signal.<sup>13</sup> This was observed directly on the meter reading of the lock-in amplifier.

The solutions used in the experiments were all prepared from either AnalaR or SpectrosoL grade reagents (BDH) and were diluted with triply distilled water.

The variables and their boundary conditions for the optimisations and the step sizes for the AVS method are shown in Table 1 for the emission studies and Table 2 for the fluorescence studies. The boundary conditions were set at the limits for ease of plasma operation, as chosen by experienced operators. For example, with emission a plasma gas flow-rate of lower than 0.3 l min<sup>-1</sup> caused the plasma tube to burn, but a plasma gas flow-rate of greater than 2 l min<sup>-1</sup> extinguished the plasma.

The computer program used for the simplex method was modified slightly to incorporate a sub-routine to record the SBR, to be called upon when the main program required a value of the response factor. The variable names were entered into the computer program with the ranges shown in Table 1 from which the program calculated the initial simplex from the boundary conditions. Also entered was the required relative standard deviation (RSD) for termination. A value of 3% was used as this was comparable to twice the standard deviation (2s) value that had been used in the AVS method.

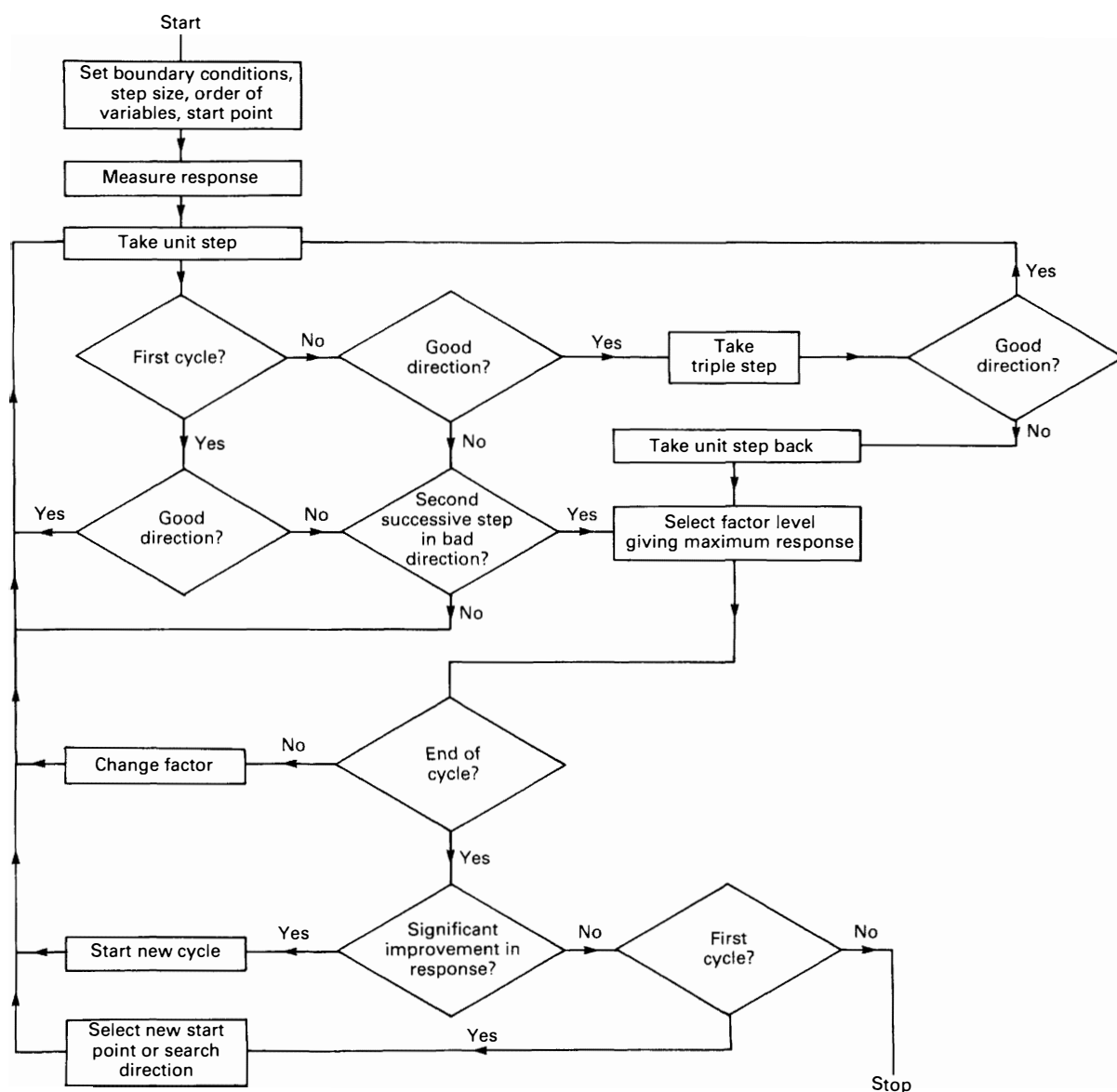


Fig. 2. Flow diagram for the hybrid AVS method

### Model Data

All three AVS methods were used on a model two-factor response surface.<sup>2</sup> The response,  $R$ , was calculated from

$$R = 20 + 0.8F(1) + 0.8F(2) + \frac{0.22F(1)F(2)}{0.015F(1)^2 - 0.015F(2)^2} + E$$

where  $F(1)$  and  $F(2)$  are the values of the response factors and  $E$  is an error term taken randomly from a normally distributed population with a mean of zero and of unit variance. This function has a maximum value of 100 where  $F(1) = F(2) = 100$ . The starting point was 20,20 and two initial step sizes were used, 5 and 10. Although these values are all integers and favour AVS, the variable step size methods rapidly go to non-integral values and the calculated response has an added random component.

### Atomic Emission Spectrometry

The hybrid AVS method and the simplex method were used. Lead ( $10 \text{ mg l}^{-1}$ , 405.78 nm), sodium ( $1 \text{ mg l}^{-1}$ , 589.0 nm), calcium ( $1 \text{ mg l}^{-1}$ , 422.67 nm) and aluminium ( $10 \text{ mg l}^{-1}$ , 396.15 nm) were used as test elements.

The AVS method is sometimes criticised because the order in which the variables are taken may significantly influence the progress of the search. Hence, all possible permutations of the

order of the variables were used for the AVS optimisation of the instrument for lead. As there were five variables, a total of 120 AVS optimisations were performed. The order of the variables for the optimisation of the response for the other three elements was chosen after the results for the lead experiments had been examined for a suitable order. As a further check on the suitability of this particular order of variables, AVS optimisations for manganese ( $10 \text{ mg l}^{-1}$ , 279.48 nm), tin ( $100 \text{ mg l}^{-1}$ , 326.23 nm) and calcium ionic emission ( $1 \text{ mg l}^{-1}$ , 393.36 nm) were performed.

### Atomic Fluorescence Spectrometry

Calcium ( $1 \text{ mg l}^{-1}$ , 422.7 nm) and copper ( $1 \text{ mg l}^{-1}$ , 324.8–327.8 nm) were used as the test elements. The order of the variables for the AVS method were as given in Table 2 and the same simplex method was used with all nine variables. The same criteria for stopping were used for each method as were used for the atomic emission experiments.

## Results and Discussion

### Model Response Surface

The performance of the three AVS methods for the two different step sizes is shown in Table 3 together with the

**Table 1.** Boundary conditions and step size for the AVS method for emission studies

Variable	Range	Step size
Plasma gas flow/l min <sup>-1</sup>	0.3–2	0.1
Injector gas flow/l min <sup>-1</sup>	0.5–1.5	0.1
Coolant gas flow/l min <sup>-1</sup>	9–20	1
Power in the plasma*/kW	485–930	30
Viewing height above the coil/cm	3.1–6.2	0.1

\* Measured by insertion of a dummy load into the work coil.

**Table 2.** Boundary conditions and step size for the AVS method for fluorescence studies

Variable	Range	Step size
<i>Source plasma—</i>		
Injector gas flow/l min <sup>-1</sup>	0.8–3.6	0.2
Plasma gas flow/l min <sup>-1</sup>	20–30	1
Coolant (air) flow/l min <sup>-1</sup>	30	Fixed
Power in the plasma*/kW	2.6–6.5	0.3
Position of the coil below the optical axis/cm	1–5	0.1
<i>Atomiser plasma—</i>		
Injector gas flow/l min <sup>-1</sup>	1–3.6	0.2
Coolant gas flow/l min <sup>-1</sup>	8–20	1
Power in the plasma*/kW	422–771	30
Viewing height above the coil/cm	7–12	0.1
Solution uptake rate/ml min <sup>-1</sup>	1.3–5.0	0.1

\* Measured by insertion of a dummy load into the work coil.

performances of fixed<sup>11</sup> and variable step size simplex methods.<sup>10</sup>

The progress of the three AVS methods is shown in Fig. 3. It can be seen that although all methods locate the maximum, methods incorporating a variable step size are probably more accurate. The performance of the Rosenbrock method<sup>9</sup> is largely independent of the initial step size and although the method locates the maximum rapidly (on the 15th step for a search with initial step size 10), the search takes a long time to confirm that this value is indeed the maximum. The Rosenbrock method also moves rapidly and thus there is a danger that the factor space is not searched very efficiently during the initial stages of the search. There is also a danger that the maximum lies behind the point at which the step size begins to contract and a greater degree of confidence in the accuracy would be obtained if the search algorithm included a search in the two opposite directions. This would considerably extend the time required. The hybrid method was designed as a compromise between the requirements of accuracy and speed.

It should be noted that the fixed step size simplex performs very poorly<sup>15</sup> and although the variable step size method appears to be a considerable improvement in terms of speed, a comparison of the number of vertices with the number of steps of an AVS method is not an appropriate method of assessing the relative speeds of the two methods as, in general, each new vertex of the simplex requires both variables to be changed.

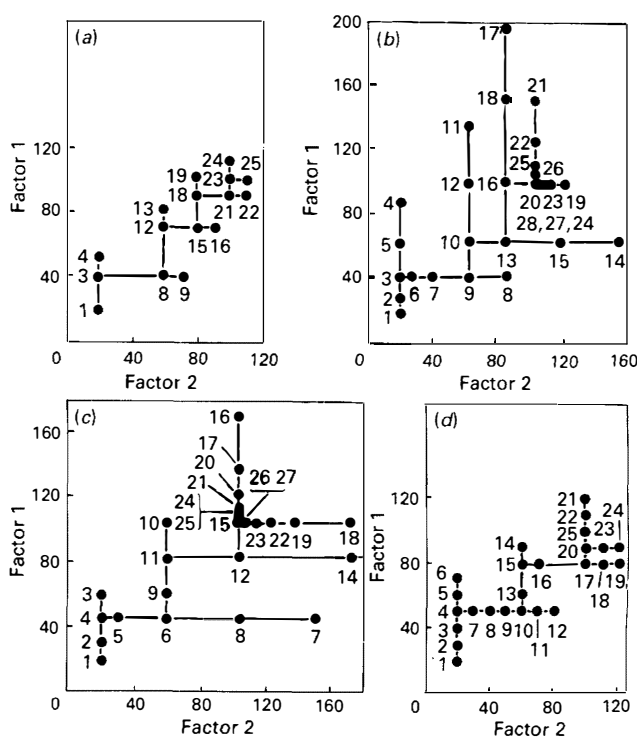
One advantage that the AVS methods have over the simplex methods is that at the end of the search, information about the shape of the response surface is available in a form that the analytical chemist requires. For example, in a study of the differences in behaviour of a nitrogen-cooled inductively coupled plasma (ICP) and an argon-cooled ICP, and of the possible reasons for the observed differences,<sup>6</sup> the experimental strategy was to optimise the five variables (injector, plasma and coolant gas flows, observation height and power coupled into the plasma) using a manually calculated simplex procedure of the type described under Experimental. This done, univariate searches of variable step size were conducted either side of the optimum value for each factor. Between seven and eleven points were taken for each variable giving rise to an additional 44 points. These univariate searches were then used as the basis for the discussion of the effects of the individual

**Table 3.** Results obtained with the model response surface

Method	Step size	No. of steps	No. of vertices	No. of changes of variable	Optimum value achieved
Fixed AVS-1	5	35	—	40	97
Fixed AVS-1	10	24	—	29	101
Fixed AVS-2	10	32	—	37	101
Rosenbrock AVS	5	28	—	35	100
Rosenbrock AVS	10	27	—	33	101
Hybrid AVS	5	43	—	49	101
Hybrid AVS	10	25	—	30	101
Fixed simplex	—*	—	56	69	97
Variable simplex	—†	—	20	37	99

\* An equilateral triangle of side 5 was used.

† The initial simplex was the same as for the fixed simplex method.



**Fig. 3.** AVS searches of model factor space (a) fixed AVS-1 with step size 10, (b) Rosenbrock AVS with initial step size 5, (c) Rosenbrock AVS with initial step size 10 and (d) hybrid AVS with initial step size 10

variables and also to confirm the success of the simplex optimisation.

More information of this sort is available from the AVS methods which change direction after only two poor responses have been obtained. Hence, this criterion was incorporated into the hybrid method. Unlike the Rosenbrock method,<sup>9</sup> the hybrid method gives evenly spaced data points in the univariate searches from the optimum value. However, the Rosenbrock method appears to have the advantage that the speed of the search is much less dependent on the initial step size than the other types of AVS method. On the other hand there is the danger, discussed earlier, of the search terminating on a ridge when the step size is large compared with the spacing between contours. If such a situation is encountered, the search would be slowed down considerably and the step size contracted until a step size had been found which allowed the search to continue. Progress on such a ridge would be very slow<sup>15</sup> and in such situations a modified simplex method would undoubtedly be a better strategy for searching the factor space. This problem of termination on a sharp ridge is not

encountered here as the response surface is sloping gently compared with the step sizes chosen. Of course, it is always possible to conceive of response surfaces which will defeat any search algorithm. Very high, sharp maxima, for example, will be difficult to locate. Previous studies of the SBR response surface in the region of the optimum for ICP-AES<sup>6</sup> indicate that the surface does not contain features of this sort.

### Atomic Emission Spectrometry

The progress of the AVS experiments is summarised in Table 4. The order of the variables was selected from the result of studying all 120 orders for the optimisation of the instrument for lead. As can be seen from the table, apart from sodium and aluminium this order gave at least 70% of the maximum SBR at the end of the first cycle.

Each of the 120 lead optimisations gave the same SBR of 3.01, with 14 requiring four cycles before termination and 106 requiring three cycles. The average time for an optimisation was 2 h with about 45 min spent on the first cycle. The progress made after the first cycle is summarised in Fig. 4, which shows that the majority of optimisations achieve at least 70% of the maximum SBR at this stage.

The progress of the AVS method is shown in Fig. 5 as a graph of the current maximum SBR against step number. As each step represents one (sometimes two) change(s) of variable value, the number of steps is a good guide to the number of changes of variable that were required. Similar graphs are given in Fig. 6 for the simplex optimisations of the same elements. It is thought that these graphs provide more useful information than the generally accepted way of presenting such results,<sup>16</sup> which is shown in Fig. 7 as the normal "map" of the progress of the simplex. However, such maps do not show the composition of the current simplex and it is not possible to see (a) how fast the simplex is moving towards an optimum or (b) how close the simplex might be to termination. In addition to showing the progress as a function

of the vertex number, the abscissae also show the number of changes of variable. The optimised conditions and corresponding SBRs are given in Table 5. The values may be compared with the corresponding entries in Table 4 at the end of the third cycle for the corresponding elements. The optimum values of the variables are slightly different and the final SBR is slightly lower for the simplex than for the AVS methods. This may be due to the fact that the optimum conditions given by the simplex method are those corresponding to the vertex giving the highest SBR in the final simplex, whereas calculation of the centroid of the final simplex as for some modifications<sup>5</sup> of this method may produce slightly better results. The simplex methods took, on average, 2 h to reach termination conditions, but because of the way the simplex searches the factor space, stopping the search at about vertex 7 or 8 (analogous to one cycle of a three-cycle AVS optimisation) it would probably not give such good progress towards the optimum as the AVS method at the same stage. This is because the first six vertices are required to define the initial simplex and thus vertices 7 and 8 are only the first two permitted moves. A problem in terminating the simplex method is seen for Ca and Na for which optimum conditions are found well before the criteria for termination are satisfied. This is analogous to the situation illustrated for the Rosenbrock AVS method [Fig. 3(c)] and is a problem common to all variable step size search algorithms. This particular version of the simplex program used did not recognise when a suggested vertex lay outside the boundary conditions and thus some time was lost, as typically several vertices of this type would be proposed during the implementation of the simplex method.

The progress of the simplex method is shown in detail in Table 6 for sodium from which it can be seen that an invalid vertex was suggested on some 13 occasions and on 9 occasions the so-called " $K + 1$  rule" was invoked to check on the validity of a response at a vertex which had occurred in  $K + 1$  ( $K$  is the number of variables) successive simplexes (not counting the one with which the vertex first appeared) without being

Table 4. Progress of AVS searches using best order of variables

Element	Status	Injector gas flow/ l min <sup>-1</sup>	Coolant gas flow/ l min <sup>-1</sup>	Height/ cm	Power/ kW	Plasma gas flow/ l min <sup>-1</sup>	SBR	Maximum after 1st cycle, %
Pb	Start	0.5	20	3.5	485	2.0	1.08	
	End 1st cycle	0.9	15	4.5	612	0.5	2.58	86
	End 2nd cycle	1.0	11	4.6	612	0.3	2.97	
	End 3rd cycle	1.0	11	4.6	644	0.3	3.01	
Na	Start	0.5	20	3.1	485	2.0	1.43	
	End 1st cycle	1.0	17	4.8	517	2.0	20.6	37
	End 2nd cycle	1.5	12	4.8	580	2.0	55.9	
	End 3rd cycle	1.5	11	4.8	549	2.0	56.7	
Al	Start	0.5	20	3.1	485	2.0	1.10	
	End 1st cycle	0.7	17	4.6	549	2.0	2.97	62
	End 2nd cycle	1.0	12	4.8	803	2.0	4.73	
	End 3rd cycle	1.0	11	4.7	739	2.0	4.79	
Ca <sup>I</sup>	Start	0.5	20	3.1	485	2.0	1.01	
	End 1st cycle	0.9	16	4.6	612	2.0	4.63	70
	End 2nd cycle	1.2	12	4.7	612	2.0	6.58	
	End 3rd cycle	1.2	11	4.7	612	2.0	6.63	
Ca <sup>II</sup>	Start	0.5	20	3.1	485	2.0	1.22	
	End 1st cycle	0.5	20	4.4	549	2.0	2.55	73
	End 2nd cycle	0.5	19	4.5	676	1.3	3.42	
	End 3rd cycle	0.6	19	4.5	676	1.1	3.48	
Mn	Start	0.5	20	3.1	485	2.0	1.17	
	End 1st cycle	0.8	18	4.6	549	2.0	5.75	87
	End 2nd cycle	1.0	16	4.6	549	1.1	6.58	
	End 3rd cycle	1.0	16	4.6	549	1.0	6.61	
Sn	Start	0.5	20	3.1	485	2.0	1.48	
	End 1st cycle	0.7	19	4.4	517	2.0	4.00	89
	End 2nd cycle	0.8	18	4.4	549	2.0	4.43	
	End 3rd cycle	0.8	16	4.4	517	2.0	4.48	

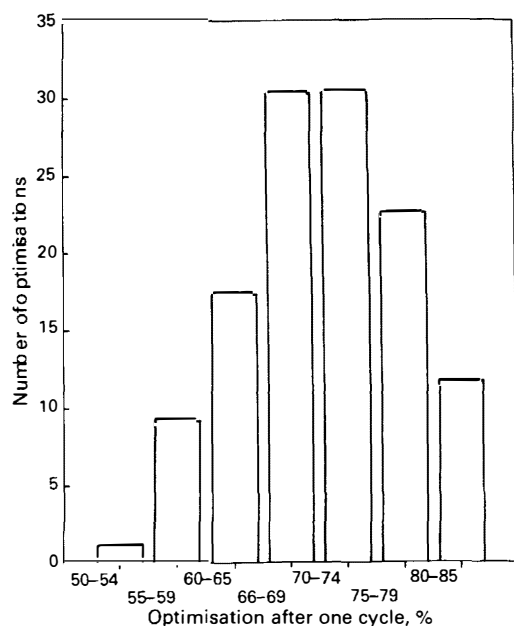


Fig. 4. Progress of hybrid AVS optimisations after one cycle

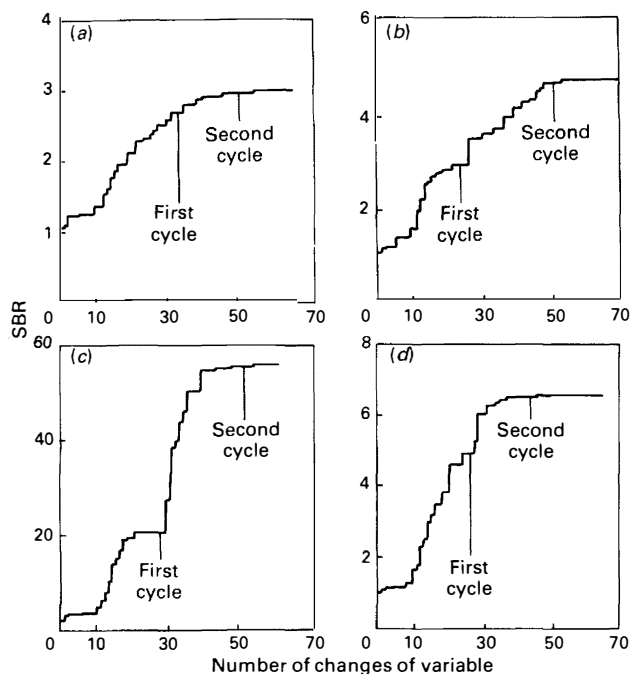


Fig. 5. Progress of hybrid AVS method of optimisation as a function of the number of changes of variable for (a) lead, (b) aluminium, (c) sodium and (d) calcium

eliminated. In order to save time these “ $K + 1$ ” checks were omitted. Values in italics in the table indicate the value of a parameter outside the boundary conditions. When this occurred the appropriate entry was made via the keyboard and the program calculated a new vertex. Not counting the initial vertex, there would have been 145 changes of variable if the checks had been included. In practice 109 changes of variable were made. This may be compared with the progress of the hybrid AVS method, shown in Table 7, which requires 75 changes of variable before termination. The additional information available from the AVS method is illustrated by Fig. 8. Further points have been added to these curves to give a more comprehensive picture of the variation of the response with each variable.

The plots for the first and second cycles also contain useful information in that they demonstrate to the operator to what

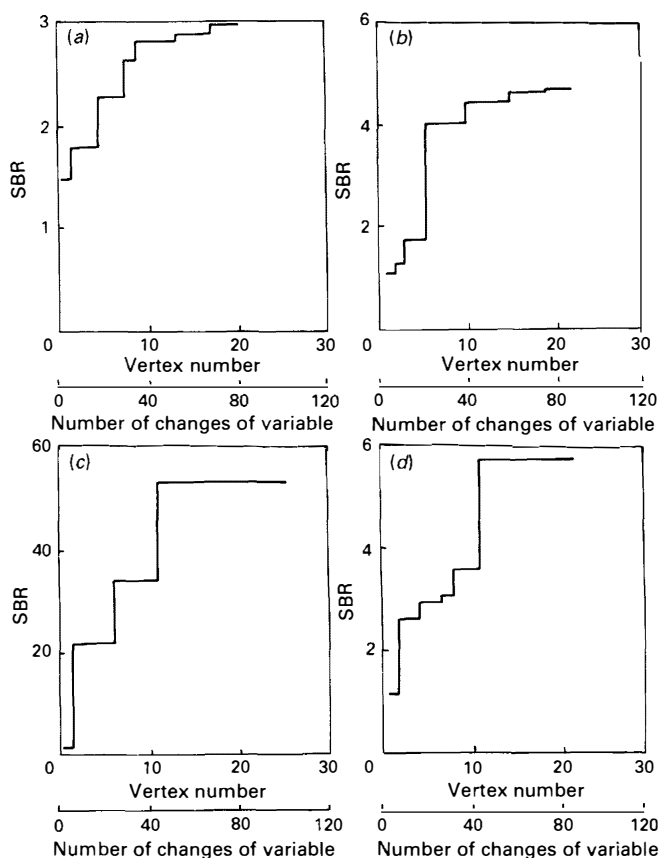


Fig. 6. Progress of the simplex method of optimisation as a function of the vertex number and number of changes of variable for (a) lead, (b) aluminium, (c) sodium and (d) calcium. The SBR value is the current optimum

Table 5. Optimum conditions obtained with the simplex method

Element	Injector gas flow/ l min <sup>-1</sup>	Coolant gas flow/ l min <sup>-1</sup>	Height/ cm	Power/ W	Plasma gas flow/ l min <sup>-1</sup>	SBR	
Pb	..	1.0	12.8	4.6	644	0.9	2.97
Al	..	1.1	13.1	4.8	771	1.3	4.61
Na	..	1.4	12.8	4.8	517	1.6	52.9
Ca	..	1.1	13.9	4.9	612	1.1	5.62

extent the response is dependent on a particular variable and they give some impression of the shape of the cross-sections through the factor space parallel to each variable axis.

Most previous studies of the simplex optimisation of ICP atomic emission spectrometry (AES) do not give details of the time involved so a comparison with previous studies is difficult. For example, in a comparison of two sample introduction configurations reported recently,<sup>7</sup> a manually calculated simplex optimisation of three variables (injector flow, power and observation height) was followed by approximately an additional 20 points in three univariate searches from the simplex optimised conditions. A four-parameter optimisation of a nitrogen-cooled argon ICP for maximum SBR and minimum matrix interference was stated<sup>17</sup> to have taken 2 h. However, the algorithm used required an experienced operator to determine when the SBR initially used as the response had achieved a maximum and then to change to the minimum interference response function. This was terminated when “the response function (recorded as a maximum for graphical purposes) appeared to have reached a maximum and the composite SBR had not decreased too much.” Hence again, an experienced operator was needed to decide when to terminate the whole process. It was not obvious on what basis the operator would make a decision as the graphs of the

**Table 6.** Progress of simplex optimisation algorithm for sodium. Values in italics are suggestions for points which lie outside the boundary conditions

Vertex number	Attempted move*	Injector gas flow/ l min <sup>-1</sup>	Coolant gas flow/ l min <sup>-1</sup>	Height/ cm	Power/ W	Plasma gas flow/ l min <sup>-1</sup>	SBR	Vertices in current simplex
1	I	0.5	9	3.1	485	0.3	1.35	
2	I	1.5	11.9	3.7	580	0.6	20.8	
3	I	0.8	19.9	3.7	580	0.6	7.15	
4	I	0.8	11.9	6.0	580	0.6	9.78	
5	I	0.8	11.9	3.7	866	0.6	3.49	
6	I	0.8	11.9	3.7	580	1.9	15.11	1,2,3,4,5,6
7	R	1.4	17.8	5.2	739	1.4	20.4	2,3,4,5,6,7
	R	1.3	17.3	5.2	295	1.4		
8	C <sub>w</sub>	0.9	13.2	4.0	707	0.8	11.1	2,3,4,6,7,8
	R	1.4	7.0	5.3	644	1.5		
9	C <sub>w</sub>	0.9	16.5	4.1	612	0.9	8.78	2,4,6,7,8,9
	R	1.4	16.6	2.5	612	1.6		
10	C <sub>w</sub>	1.0	13.0	5.0	612	0.9	15.4	2,4,6,7,8,10
11	R	1.3	10.6	4.6	644	1.4	33.9	2,6,7,8,10,11
	E	0.2		0.2		0.3		
12	R	1.4	12.8	4.8	517	1.6	52.9	2,6,7,10,11,12
	Ch(2)	1.5	11.9	3.7	580	0.6		2,6,7,10,11,12
	Ch(6)	0.8	11.9	3.7	580	1.9		2,6,7,10,11,12
	R	2.0	14.6	5.6	612	0.6		
13	C <sub>w</sub>	1.0	12.5	4.2	549	1.5	15.0	2,7,10,11,12,13
	Ch(7)	1.4	17.8	5.2	739	1.4		2,7,10,11,12,13
	R	1.8	13.2	4.0	612	0.8		
14	C <sub>w</sub>	1.1	13.1	4.8	580	1.4	39.8	2,7,11,12,13,14
	R	1.7	13.9	5.0	612	1.0		
15	C <sub>w</sub>	1.2	12.8	4.4	580	1.4	38.6	2,7,11,12,14,15
	R	1.2	6.7	3.6	440	1.0		
16	C <sub>w</sub>	1.3	15.0	4.8	644	1.3	46.6	2,11,12,14,15,16
	R	1.0	13.9	5.6	580	2.1		
17	C <sub>w</sub>	1.4	12.4	4.2	580	1.0	37.4	11,12,14,15,16,17
	Ch(11)	1.3	10.6	4.6	644	1.4		11,12,14,15,16,17
18	R	1.3	15.8	4.6	517	1.2	49.5	12,14,15,16,17,18
	Ch(12)	1.4	12.8	4.8	517	1.6		12,14,15,16,17,18
	R	1.2	15.5	5.2	455	1.6		
19	C <sub>w</sub>	1.4	13.1	4.4	580	1.2	45.3	12,14,15,16,18,19
	Ch(14)	1.1	13.1	4.8	580	1.4		12,14,15,16,18,19
20	R	1.4	15.1	5.0	580	1.2	48.5	12,14,16,18,19,20
	R	1.7	15.9	4.7	485	1.5		
21	C <sub>w</sub>	1.2	13.7	4.7	580	1.2	48.0	12,16,18,19,20,21
	Ch(16)	1.3	15.0	4.8	644	1.3		12,16,18,19,20,21
22	R	1.3	15.8	5.1	517	1.5	48.0	12,16,18,20,21,22
	R	1.3	14.3	4.9	412	1.3		
23	C <sub>w</sub>	1.3	14.8	4.9	612	1.3	49.0	12,18,20,21,22,23
24	R	1.5	16.0	5.0	549	1.5	51.1	12,18,20,22,23,24
	Ch(18)	1.3	15.8	4.6	517	1.2		12,18,20,22,23,24
	Ch(12)	1.4	12.8	4.8	517	1.6		12,18,20,22,23,24
25	R	1.4	14.0	4.6	517	1.3	49.0	12,18,20,23,24,25
26	R	1.4	14.9	4.9	549	1.4	50.2	12,18,20,23,24,26

\* C<sub>w</sub> = contraction, E = expansion, R = reflection, Ch = check as vertex appeared in K + 1 successive simplexes.

response function shown did not indicate which of the vertices comprised the current simplex.

In the studies reported here no evidence for dual optima was obtained, although it is known that these can occur with nitrogen-cooled plasmas. Under such circumstances it has been observed<sup>18</sup> that a simplex method could become "stranded at a false optimum" (in the same report it was indicated how these could be overcome using the rules of simplex), an AVS method used to search the same factor space did not, apparently, suffer from this problem. With AVS the result can be seen instantly and continuous measurement is possible. It is also possible to sweep the variables throughout their physically realisable range and hence get rid of the problems of scale. False optima can be tested for by taking the variables in pairs.

### Atomic Fluorescence Spectrometry

The results obtained for the AVS optimisation are shown in Table 8. These values were obtained after two cycles which

took approximately 45 min. The reason for the increase in speed over the same optimisation for the emission mode is that the value of the response (total fluorescence signal) is viewed directly on the lock-in amplifier and no calculation is involved.

The progress of the simplex method is shown in Fig. 9. The simplex was unable to satisfy the criteria for termination and the values shown represent the progress of the simplex over a 4-h period. The values obtained from the best vertex during this period are given in Table 9. A comparison of the signal values given in Tables 8 and 9 show that although there is reasonable agreement between the two optimisation strategies for calcium, the simplex was unable to find an optimum for copper, although, as pointed out for emission work,<sup>17</sup> an experienced operator would be able to decide when to terminate the simplex. For fluorescence spectrometry the response surface may be very steep in the direction of some of the variables. This presents few problems for the AVS method when there is direct visual feedback of the figure of merit as the step size may be readily reduced to search the factor space at an appropriate speed.<sup>15</sup>



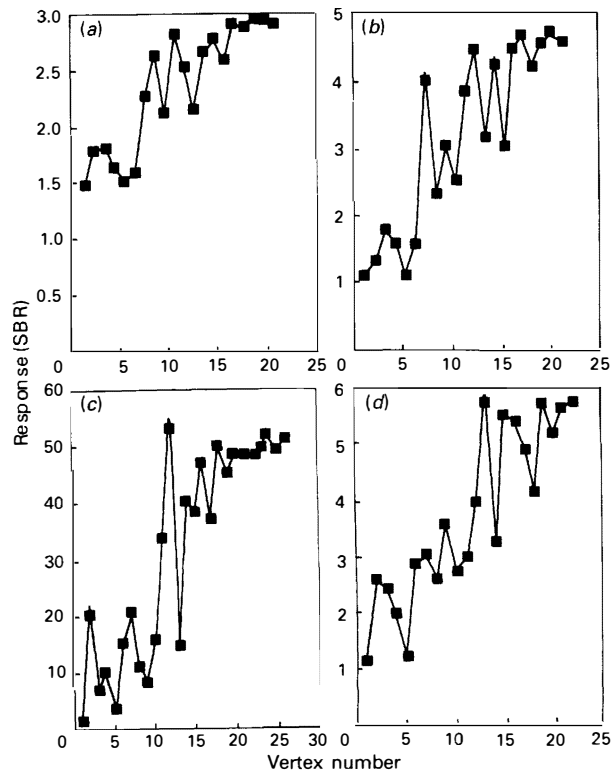


Fig. 7. Map of simplex response (graph of SBR against vertex number) for (a) lead, (b) aluminium, (c) sodium and (d) calcium

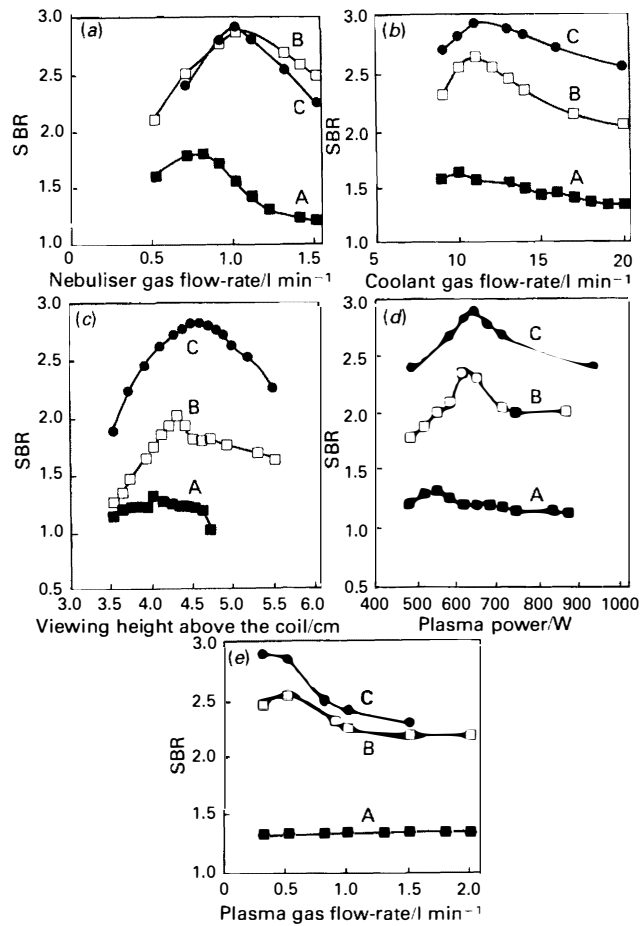


Fig. 8. Full exploration of factor space for lead. A, 1st cycle; B, 2nd cycle; and C, 3rd cycle

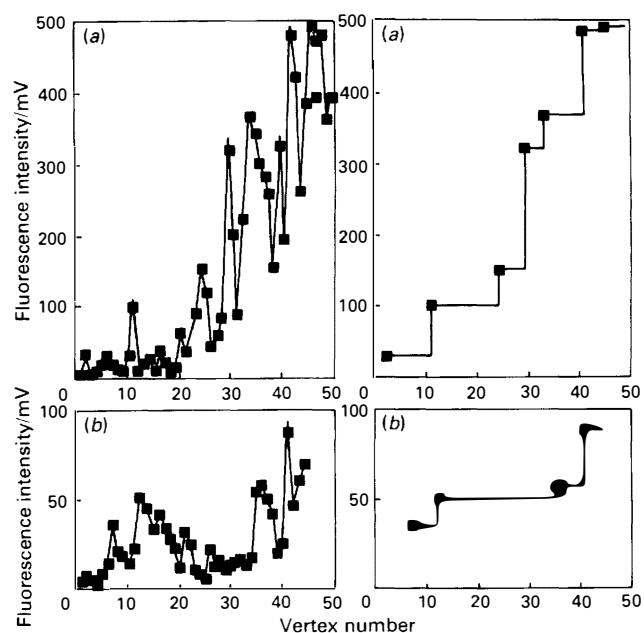


Fig. 9. Progress of simplex optimisation for atomic fluorescence. (a) Calcium and (b) copper

Table 7. Progress of the AVS method for sodium

	Injector gas flow/ l min <sup>-1</sup>	Coolant gas flow/ l min <sup>-1</sup>	Height/ cm	Power/ W	Plasma gas flow/ l min <sup>-1</sup>	SBR
Original conditions starting 1st cycle	0.5	20	3.1	485	2.0	1.43
	0.6					1.63
	0.9					2.73
	1.0					3.04
	1.1					3.04
	1.2					2.88
	1.3					2.61
	1.0	20				3.04
		19				3.08
		17				3.29
		16				2.91
		15				2.79
	1.0	17	3.1			3.29
			3.2			4.55
			3.5			6.02
			3.6			7.51
			3.9			10.10
			4			13.77
			4.3			14.91
			4.4			16.62
			4.7			18.82
			4.8			19.30
			4.9			18.91
			5			17.81
			5.1			17.62
	1.0	17	4.8	485		19.30
				517		20.60
				549		18.81
				580		18.12
				612		17.68
	1.0	17	4.8	517	2	20.60
					1.9	19.36
					1.8	14.1
					1.3	12.92
End of 1st cycle	1	17	4.8	517	2	20.60
Starting 2nd cycle	1					20.60
	1.1					27.55
	1.4					38.71
	1.5					40.05

Table 7. continued—

	Injector gas flow/ l min <sup>-1</sup>	Coolant gas flow/ l min <sup>-1</sup>	Height/ cm	Power/ W	Plasma gas flow/ l min <sup>-1</sup>	SBR
		16				44.16
		13				46.43
		12				50.87
		11				39.52
		10				36.75
		9				35.84
			4.7			49.39
	1.5	12	4.8			50.87
			4.9			50.16
			5			48.24
	1.5	12	4.8	517		50.87
				549		55.30
				580		55.90
				612		53.51
				644		51.88
				676		
	1.5	12	4.8	580	2	55.90
					1.9	53.69
					1.8	52.56
					1.2	39.52
End of 2nd cycle . . . . .	1.5	12	4.8	580	2	55.90
Starting 3rd cycle . . . . .	1.5					55.90
	1.4					49.85
	1.5	12				55.90
		11				56.18
		10				53.56
		9				51.59
	1.5	11	4.8			56.18
			4.9			54.91
				517		55.11
				549		56.68
	1.5	11	4.8	580		56.18
				612		53.64
	1.5	11	4.8	549	2	56.68
					1.9	54.43
End of 3rd cycle . . . . .	1.5	11	4.8	549	2	56.68

Table 8. Optimum plasma parameters (ASIA instrument) obtained with AVS method in the fluorescence mode

Element	Wavelength/nm	Source plasma					Atomiser plasma					Fluorescence signal for 1 p.p.m./mV	
		Injector gas flow/ l min <sup>-1</sup>	Height above the coil/cm	Power in the plasma/ kW	Plasma gas flow/ l min <sup>-1</sup>	Coolant gas flow/ l min <sup>-1</sup>	Injector gas flow/ l min <sup>-1</sup>	Viewing height above the coil/cm	Power in the plasma/ W	Coolant gas flow/ l min <sup>-1</sup>	Sample uptake/ ml min <sup>-1</sup>		Slit width/nm
Ca . . .	422.7	3.1	2	6.2	25	Air 30 fixed	2	9.7	485	11	3.8	3.6	495
Cu . . .	Σ 324.8–327.8	3.6	2	6.2	30	Air 30 fixed	3.6	11	485	10	3.8	3.6	285

The hybrid AVS method, as shown in Fig. 2 appears rather complicated but, in practice, as the operator becomes more experienced, the rules for step size and direction changing could be varied at the operator's discretion thus considerably increasing the speed of the method. In fact the variable can be scanned continuously at an appropriate speed already stated. Hence an automatic system using a peak-finding device may be possible.

**Conclusions**

As far as optimisation of ICP-AES is concerned, a cyclic, variable step size univariate search method of the factor space

is as efficient as the simplex method in terms of the optimum found and of the time taken, but offers the advantage that univariate information about the effect of each factor is available in a readily understandable form and hence aids the inexperienced operator of such instrumentation. The order in which the variables are taken does not appear to be important. In many applications the percentage maximum after the first cycle would suffice, *i.e.*, a single univariate search.

With regard to ASIA, the AVS method performs significantly better than the simplex method, which cannot take advantage of the benefits of immediate visual feedback of the value of the figure of merit on this apparatus.

More information on the progress of a simplex method is available if the current optimum is plotted against vertex

**Table 9.** Plasma parameters (ASIA instrument) obtained with simplex method after 48 vertices

Element	Wavelength/nm	Source plasma					Atomiser plasma					Fluorescence signal for 1 p.p.m./mV	
		Injector gas flow/ l min <sup>-1</sup>	Height above the coil/cm	Power in the plasma/ kW	Plasma gas flow/ l min <sup>-1</sup>	Coolant gas flow/ l min <sup>-1</sup>	Injector gas flow/ l min <sup>-1</sup>	Viewing height above the coil/cm	Power in the plasma/ W	Coolant gas flow/ l min <sup>-1</sup>	Sample uptake/ ml min <sup>-1</sup>		Slit width/nm
Ca	422.7	3.2	2.4	4.2	25	Air 30 fixed	2.2	10.3	485	12.6	3.5	3.6	490
Cu	Σ324.8–327.8	2.4	3.6	3.8	26	Air 30 fixed	2.6	6.6	517	11.2	4.2	3.6	89

number rather than the response at each vertex. Most information is obtained if both plots are given.

It is stressed that the conclusions drawn from the results of this study may only apply to inductively coupled plasma atomic emission and atomic fluorescence spectrometry. Separate studies would be required before any conclusions could be drawn about the relative merits of various optimisation strategies applied to other chemical instrumentation.

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