APPENDIX A

SIMPLEX OPTIMISATION [61-64]

The sequential simplex method was first presented by Spendley et al and later applied to analytical chemistry by Long who used the simplex method to optimise the colourimetric determination of sulfur dioxide. Deming and Morgan began to promote the procedure in 1973 when the simplex method began to find widespread use in analytical chemistry. The simplex method has also been used for mathematical modelling such as non-linear least square curve fitting.

The simplex is a geometric figure defined by a number of points equal to one more than the number of dimension of the space. A simplex in two dimension is triangular, and simplex in three dimension is a tetrahedron. The series can be extended to higher dimensions but the simplexes are not easily visualised. For purpose of illustration, two dimension simplexes will be used. The method is applicable to any number of dimensions. Optimisation will be taken to mean maximisation of response, but it could apply equally well to the process of finding a minimum.

Deming and Morgan introduced the rules of the simplex procedure for decisions required to force the simplex to move to the region of optimum response as follows :

1) *A move is made after each observation of response.* When the responses at all vertices of a simplex have been evaluated, decisions can be made as to which direction to move.

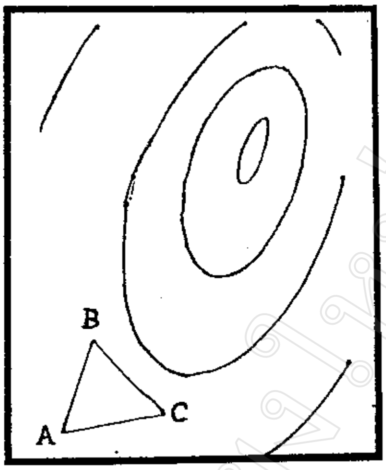


Fig. A. 1 The simplex in two dimensions (62)

2) *A move is made into that adjacent simplex which is obtained in discarding the point of the current simplex corresponding to the least variable response and replacing it by its mirror image across the face of the remaining points.*

This rules can be explained by Fig. A.2

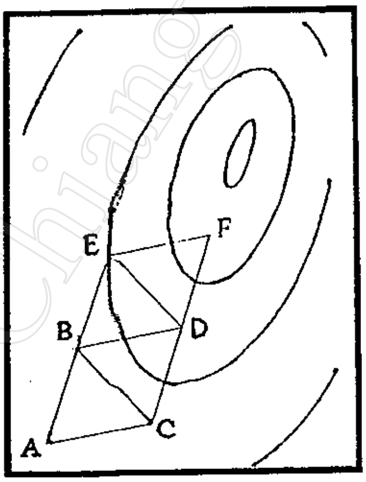


Fig. A.2 The moving in normal progression of two dimensional simplex (62)

Fig. A.2 shows the three moves in the normal progression of a two-dimensional simple toward an optimum. Point A of the origin simplex has the lowest response and is discarded, leaving points B and C. Reflection of point A across the face BC generates point D which together with point B and C form the second simplex. The response at point D is observed. Only the new observation is required to complete a new simplex. Discarding point C and reflecting gave the simplex BDE. Finally, simplex DEF is formed after eliminating point B. If the reflected point is lowest in the new simplex, rule 2 would reflect the simplex back to the previous one. The simplex would then oscillate and become stranded. This result is shown in Fig. A.3 where points E and G are both less desirable than either points F and D. An exception to rule 2 is therefore necessary.

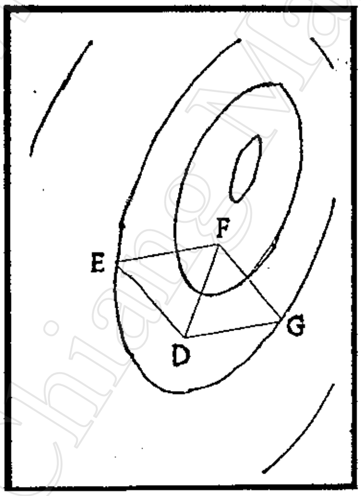


Fig. A.3 Failure of simplex on ridge (62)

3) *If the reflected point has the least desirable response in the new simplex, do not reapply rule 2, but instead rejected the second lowest response in the new simplex and continue.*

This is shown in Fig. A.4 indicating the movement of a simplex on a ridge. Rule 3 was employed between simplexes DFG and FGH and between simplexes FIJ and IJK. It is possible to perform replicate determinations at a given vertex and to use the mean of these as the response for that vertex. If the differences in response are large compared to the size of the indeterminate error, the simplex will move in the proper direction, and repetition of observations would be wasteful. If the differences are small enough to be affected by indeterminate error, the simplex may move in the wrong direction. However, a move in the wrong direction will probably yield a lower response which would be quickly corrected by rules 2 and 3.

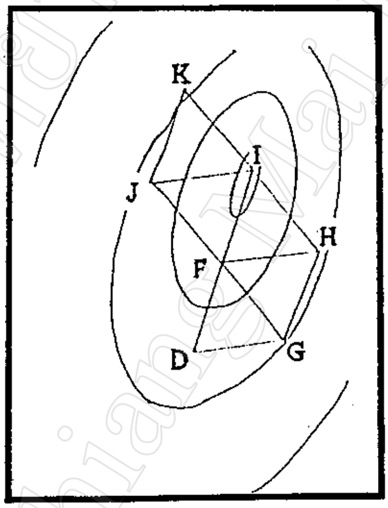


Fig. A.4 Progress of simplex on ridge (62)

4) *If a vertex has been retained in k+1 simplexes, before applying rule 2 reobserve the response at the persistent vertex.*

If the vertex is truly near the optimum, it is probable that the repeated evalution of response will be consistently high, and the maximum will be retained. If the response at the vertex was high because of an error in observation it is improbable that the repeat observation will also be high, and the vertex will eventually be eliminated.

5) *If a new vertex lies outside the boundaries of the independent variables, do not make an experimental observation, but instead assign it a very undesirable response.*

Application of rule 2 and 3 will then force the simplex back inside its boundaries, and it will continue to seek the optimum response.

Simplex optimisation find extensive use in the development of analytical methods and in optimising the performance of analytical instrumentation. This method does not use traditional testing of significance and is therefore faster and simpler than the previous sequential one-factor-at-a-time optimisation procedure. It rapidly attains the experimental optimum, guided by calculations and decisions that are rigidly specified. The simplex method is efficient and can be easily adapted to many applications. The calculations involved are trivial and are easily programmed on small digital computers for use in automated instrumentation. If computors are not available, the necessary calculation can be done quickly and easily by hand.

APPENDIX B

ADDITIONAL RESULTS : INTERFERENCE STUDY

The detail of interference studies in flow injection analysis for the determination of yttrium (section 2.3.10) are summarised in Table B.1

Table B.1 Effect of interfering ions in flow injection analysis for yttrium determination.

Ion added	Ion : Y (III) mass ratio	Peak height (mV)	% Relative error
Y^{3+}	-	350.0	0
Al^{3+}	0.1	340.5	-2.7
	0.2	338.0	-3.4
	0.5	331.0	-5.4
	1.0	311.0	-11.1
Ba^{2+}	100	330.0	-5.7
	200	321.0	-8.2
	300	310.0	-11.4
Ca^{2+}	100	335.0	-4.2
	300	316.0	-9.7
	500	305.0	-12.8
Cu^{2+}	0.3	320.0	-8.5
	1.0	302.0	-13.7
	10.0	201.0	-42.5
Cd^{2+}	10	340.0	-2.8
	100	330.0	-5.7
	500	321.0	-8.2
Ge^{4+}	5	336.0	-4.0
	10	321.0	-8.2

Table b.1 Continues...

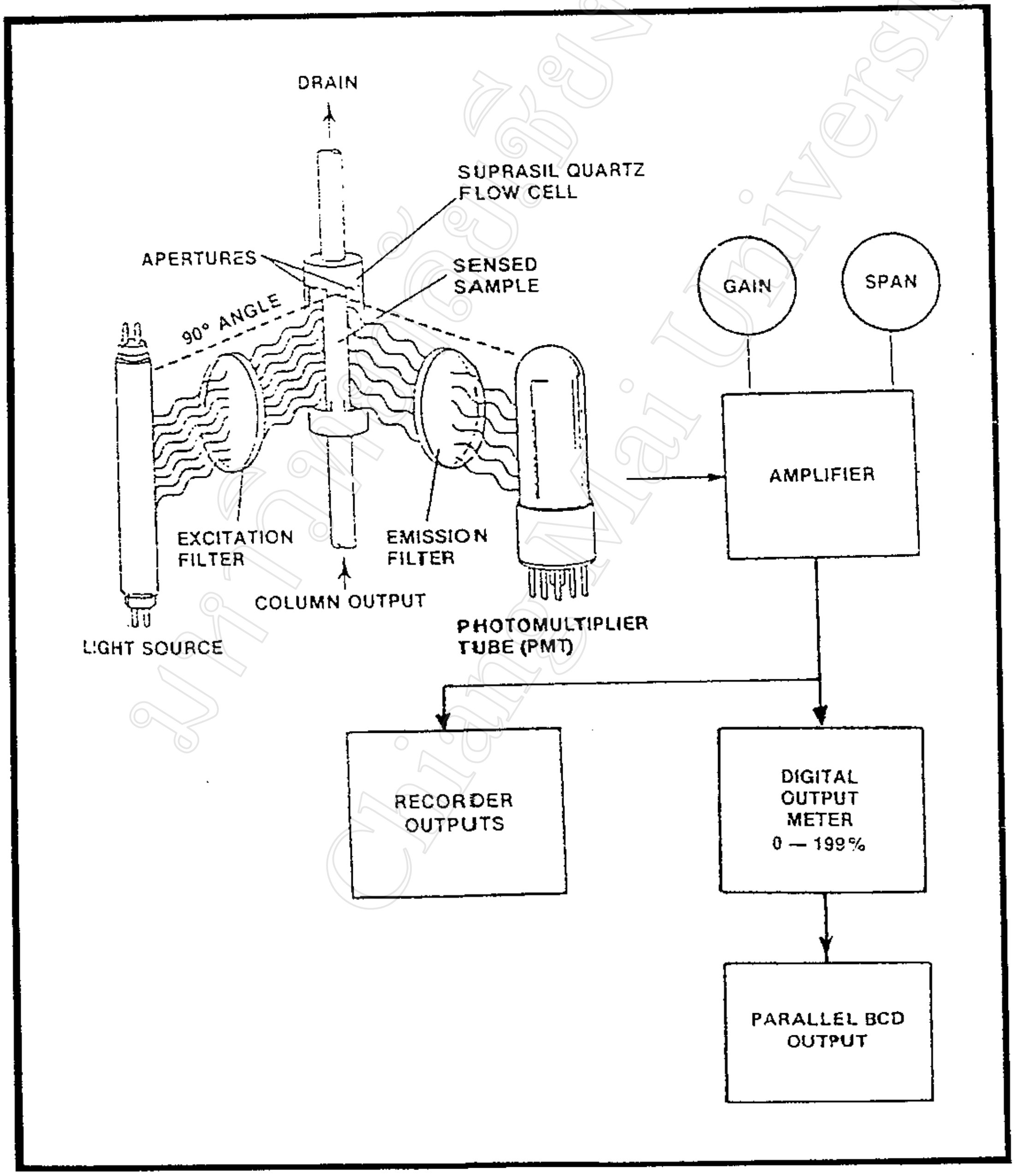
Ion added	Ion : Y (III) mass ratio	Peak height (mV)	% Relative error
La^{3+}	1.0	382.5	+9.2
Mg^{2+}	500	315.0	-10.0
	1000	305.0	-12.8
Ni^{2+}	50	325.0	-7.1
	100	305.0	-12.8
	500	255.0	-27.1
Na^{+}	1000	330.0	-5.7
	3000	315.0	-10.0
	5000	300.0	-14.2
K^{+}	100	330.0	-5.7
	1000	320.0	-8.5
	3000	316.5	-9.5
	5000	305.0	-12.8
Pb^{2+}	5	336.0	-4.0
	10	321.0	-8.2
Te^{2+}	10	338.5	-3.2
	50	336.0	-4.0
	100	340.0	-2.8
	500	398.0	-13.7
Ti^{2+}	0.1	330.0	-5.7
	0.5	315.0	-10.0
	1.0	235.0	-32.8
Zn^{2+}	1	342.0	-2.2
	5	336.0	-4.0
	10	330.0	-4.8
	30	285.0	-18.5

Table B.1 Continues..

Ion added	Ion : Y (III) mass ratio	Peak height (mV)	% Relative error
V^{5+}	5	328.5	-6.1
	10	321.0	-8.2
Co^{2+}	100	325.0	-7.1
	200	310.0	-11.4
	500	295.0	-15.7
Fe^{3+}	0.1	335.0	-4.2
	0.3	315.0	-10.0
	0.5	275.0	-21.4
CO_3^{2-}	1	342.0	-2.2
	50	315.0	-10.0
	100	290.0	-17.1
NO_3^-	1000	330.0	-4.8
	5000	320.0	-8.5
	10,000	315.0	-10.0
SO_4^{2-}	100	315.0	-10.0
	500	310.0	-11.4
	1000	305.0	-12.8

APPENDIX C

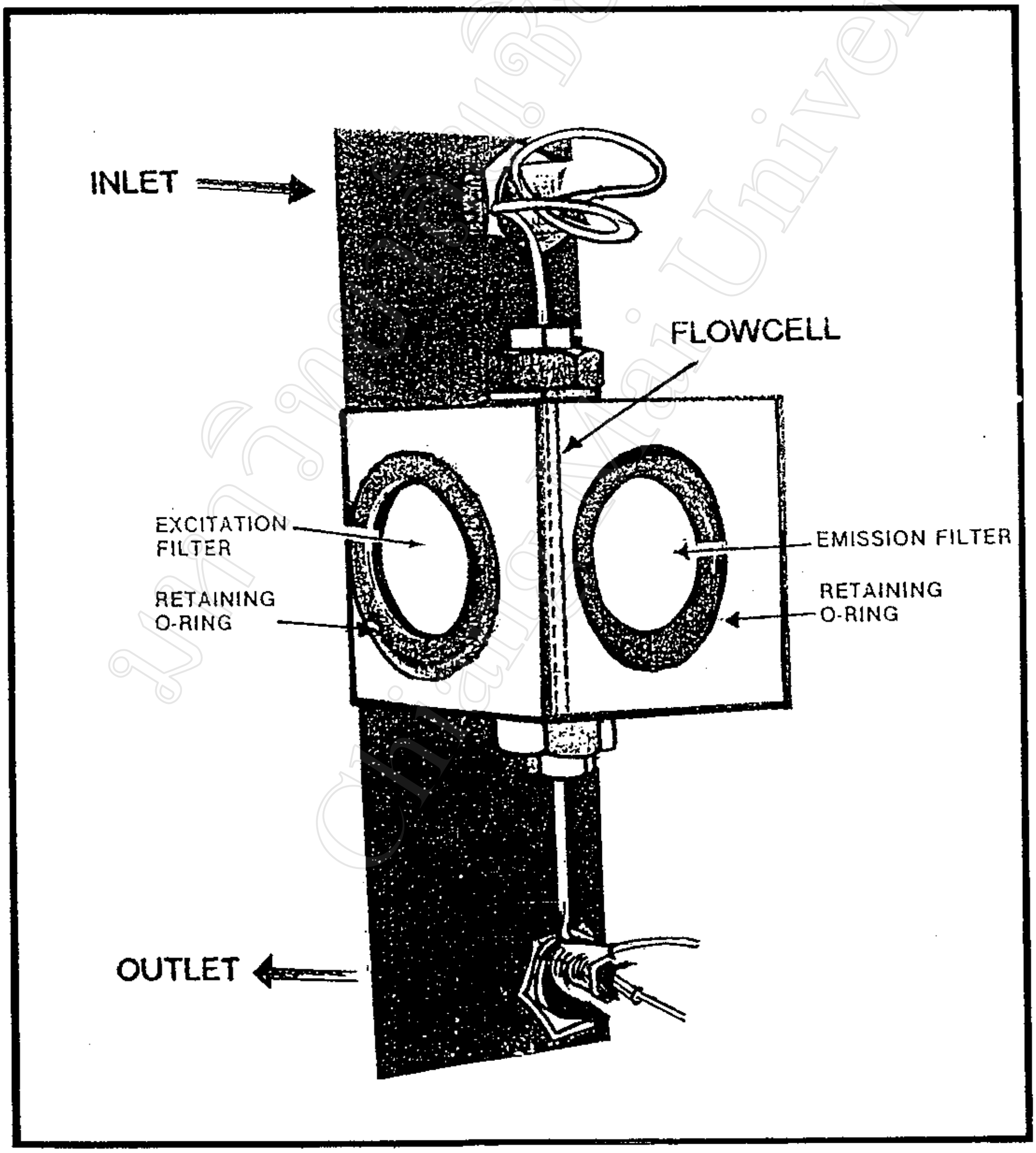
THE FLUORESCENCE DETECTOR : FUNCTIONAL DIAGRAM (MODEL 420 WATER ASSOCIATES, INC.)



APPENDIX D

THE OPTICAL FILTER OF FLUORESCENCE DETECTOR

(MODEL 420 WATER ASSOCIATES, INC.)



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