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Design and analysis of mixture systems: Applications in hydroponic, plant nutrition research

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Abstract

This study demonstrates that nutrient solutions can be defined as 'mixture systems'. A general methodology for design and analysis of mixture optimization experiments is developed. The emphasis is centered on multivariate investigation of the zone of optimal solution properties as a function of the ion composition and the total ionic strength of the solution. The study of the effects of ion interaction on well-defined solution properties is also possible by this multivariate approach. This work is a valuable tool in mineral nutritional research, because for the first time the chemical feasibility conditions of such solution, combined with additional chemical, physiological or economical constraints, form the foundation of the statistical experimental design theory, which makes the optimization of complex mixtures of ions in relation to well-defined response variables possible.

Introduction

Nutrient solutions play an important role in many fields of scientific research: plant nutrition, plant and animal tissue cultures, fermentation technology and so on. Within the last decade, the use of hydroponic installations for horticultural production has grown exponentially. The need for 'optimal' nutrient solutions is widely felt. Although different nutrient solutions have been proposed by different authors for specific situations, it seems that many investigators have chosen solutions based on trial and error approaches or based on intuitive arguments, and that, where the results have been partially successful, invariably a specific solution is recommended as being optimal for the particular situation. The fact that a given nutrient solution has seemingly desirable properties, does not necessarily rule out the possible existence of other solutions with equally desirable or better properties.

Another important argument for undertaking a systematic investigation of a nutrient system is that in many situations the user is not so much interested in finding a single point or mixture that is optimum for the system, but rather in finding a zone or group of optimal operating conditions. Finding a zone of optimal blends for a particular response or property of the solution, increases the likelihood that other properties might be optimized within this zone as well. In this context optimization means an as exact as possible description of the optimal zone as well as the boundaries of this zone.

In this study the emphasis is centered on the development of a method to optimize the nutrient solution for hydroponic plant cropping as a research tool as well as a method for commercial plant production, making use of 'mixture

theory'. Although the theory of mixture experiments dates from the late fifties and has been discussed extensively during the past two or three decades, this theory was never put to use in plant nutrition.

In this study for the first time the design and analysis of mixture experiments is applied to the problem of nutrient solutions (Schrevens, 1988).

Design and analysis of mixture experiments

The original mixture problem

The distinguishing feature of mixture experiments is that the independent variables represent proportionate amounts of the mixture rather than unrestrained amounts. These proportions must be nonnegative, and if expressed as fractions they must sum to unity. So in a q-component mixture if we let x_i be the proportion of the i-th component in the mixture, then

$$0 \leq x_i \leq 1 \text{ for } i = 1, 2, 3, \ldots q \quad (1)$$

$$\sum_{i=1}^{q} x_i = 1 \quad (2)$$

The q-components of this system are called 'mixture variables'. By virtue of the above restriction, the totality of the unrestricted factor space of q dimensions is reduced to a $(q-1)$ dimensional simplex, as was first noted by Claringbold (1955).

A most important consequence of the component dependencies in mixtures is the necessity for multivariate experimentation. This is because the effect of a single component can only be understood when studied in combination with the effects of one or more of the other components of interest. The accuracy of estimation of a single component effect increases not only with an increasing number of components but also with the design strategy used in looking at different combinations of the components.

If, in addition to the mixture variables certain other variables are present in the system where the latter variables are not bounded by the above restriction, they are called 'process variables' (Cornell, 1971; Scheffé, 1963).

In the original mixture problem developed by Scheffé (1958), the response is only a function of the proportions of the components present in the mixture and is not a function of the total amount of the mixture. In later generalizations (Piepel and Cornell, 1985; 1987), mixture models and designs where developed where the response depends on the total amount as well. In these cases the total amount could be viewed as a process variable when at the different amounts, a separate simplex or mixture design is set up and the experiments performed.

Experimentation over the whole simplex

In many mixture situations the region of interest is the whole simplex. In this case, experimental designs that have been proposed in the literature are the simplex lattice design (Scheffé, 1958), the simplex centroid design (Scheffé, 1963), the symmetric simplex design (Murty and Das, 1968), the simplex screening design (Snee and Marquardt, 1976) and axial designs (Cornell, 1975). While some of these designs are D-optimal and would be strong candidates for studying nutrient systems, most were developed in the chemical or other industries and were based on rather pragmatic and empirical grounds. For these designs specific mixture models were developed and are based on the incorporation of the mixture constraints (Eq. 1 and 2) resulting in polynomial or other model forms: Scheffé canonical polynomials (Scheffé, 1958; 1963), Cox's mixture models (Cornell, 1975; Cox, 1971) mixture models with inverse terms (Draper and St John, 1977) and adaptations of some theoretical model to the mixture situation (Gorman and Cornell, 1985).

Mixtures with additional constraints on the component proportions

Frequently chemical, physical and/or economical considerations impose additional restrictions on the component proportions. These restrictions are in the form of lower bounds $(0 < L_i \leq x_i)$ and/or upper bounds $(x_i \leq U_i < 1)$. Due to these additional constraints on the component pro-

portions, the factor space of interest is reduced to a subregion of the $(q\text{-}1)$-dimensional simplex. So, in addition to constraints 1 and 2, it is possible that the following constraints are imposed:

Single component constraints:

$$0 \leq L_i \leq x_i \leq U_i \leq 1 \tag{3}$$

Multicomponents or multivariable constraints (Snee (1976):

$$C_j \leq A_{1j}x_1 + A_{2j}x_2 + \cdots + A_{qj}x_q \leq D_j \tag{4}$$

where the L_i, U_i and A_{ij} are constants.

In situations were bounds of the form (3) are specified, it may not be possible for every component to attain its lower bound or its upper bound. In such a situation the bounds are said to be inconsistent. Piepel (1983) presented a method for checking what he called 'consistency' of the constraints in (3).

In some situations, constraints are imposed by the experimenter. For instance, if a good estimate of the optimum or sub-optimum is available and a description of the immediate vicinity of this point is needed. The aim of such experiments is twofold. Firstly when in this limited region of interest no differences in response are found, then the experiment results in the description of an optimal zone. Secondly, if significant differences are found, then by 'steepest ascent methods' the sub-optimum can be ameliorated (Box and Wilson, 1951).

In other situations the constraints (3) are inherent properties of the system, for instance dissociation, precipitation and complexation constraints of nutrient solutions.

Experimentation in constrained mixture spaces

As a result of the nature of the additional constraints (Eq. 3 and/or 4), two possibilities can occur.

1. The resulting subspace is *homomorphic* with the whole simplex. This occurs when lower bounds $L_i \leq x_i$ only are imposed or in some cases when the ranges $L_i - U_i$ of the x_i are equal in value. In such cases, the subregion is simplex shaped and the subregion is defined in terms of 'pseudocomponents' (Kurotori 1966; Crosier 1984, 1986) or 'L-pseudocomponents' (Cornell, 1990). Since the subregion is a simplex, designs used to explore a simplex region, such as the simplex-lattice or simplex-centroid designs, when expressed in the pseudocomponents, can be used.
2. The resulting subspace is a *convex, irregular hyperpolyhedron*.

In practice most mixture systems are subjected to constraints of the form (3) which results in constrained or irregularly-shaped factor spaces. In the case of an irregularly-shaped experimental region, the only way to achieve an optimal experimental design is the use of optimal design theory. For hyperpolyheders of high dimensionality computer aided design of experiments becomes essential.

The methodology to construct discrete optimal designs in constrained mixture spaces, and discussed in this work, consists of the following steps: initially one determines a list of candidate points by assuming some form of mathematical model. Then one chooses an optimal design criterion and an optimization algorithm that can be used to select a group of points from the candidate list. These steps are discussed further as:

a. To generate a list of candidate points, the 'extreme vertices' algorithm 'of Mc Lean and Anderson (1966) can be used. This algorithm generates only the extreme vertices of the irregularly-shaped hyperpolyhedron. Other algorithms that have been developed for the same purpose are XVERT (Snee and Marquardt, 1974), CONSIM (Snee, 1979), XVERT1 (Nigam et al., 1983). Once the list of extreme vertices has been generated, other boundary points such as the mid-points of the edges or the centroids of the two-dimensional faces, etc, of the hyperpolyhedron, can be defined. This list can eventually be extended with a number of interior checkpoints.

   As an alternative to generating the list of extreme vertices from which the mid-points of the edges and/or the centroids of the faces are defined, one could generate a list of candidate points by imposing a grid of points over the experimental region. This second approach, that of imposing a grid of points,

has not proven to be as successful or as popular as that of generating the extreme vertices.

b. Next comes the choice of an adequate mixture model to describe the response as a function of the mixture variables.

c. The next step is the choice of a criterion to be used to select an 'optimal' set of points from the candidate list. These points form an optimal design in the sense of allowing for the efficient estimation of the parameters in the model or for providing a value of the predicted response, assuming the functional form, with the highest degree of accuracy. For design selection, with respect to optimal parameter estimation, the following criteria have been proposed in literature: D-optimality (Kiefer and Wolfowitz, 1959; Wald, 1943), A-optimality (Elfving, 1952) and E-optimality (Ehrenfeld, 1955). To select design points for optimal response estimation the following criteria are described: G-optimality (Kiefer and Wolfowitz, 1959; Smith, 1918) and V-optimality (Fedorov, 1972; Welch, 1984). In the optimization of nutrient solutions both D- and G-optimality are used.

d. The last step is the calculation of the optimal design using exchange algorithms. These iterating procedures start with a non-singular n-point design and then add and delete one or more candidate design points in order to minimize the selection criterion, resulting in the optimal set of points. A major advantage of exchange algorithms is that they can be used to expand a given n-point design to a m-point design ($m > n$) in an optimal way, which makes optimal sequential experimentation possible. For D-optimality these algorithms were developed by Fedorov (1972) and Mitchell (1974a; 1974b). This was later extended to G- and V-optimality by Welch (1984) who made use of branch-and-bound optimization algorithms.

Several optimal design criteria have been proposed and applied on constrained mixtures (Kennard and Stone, 1966; Mitchell, 1974; 1976; Nigam et al., 1983; Snee, 1975; Snee and Marquardt, 1974; 1976; Welch, 1984; Wynn 1970; Zemroch, 1986).

The problem of nutrient solutions

In the context of this study a nutrient solution is defined as an aqueous solution of a given number of chemical substances, whose effects on a certain process are of interest. The nutrient solutions for plant growth consist exclusively of inorganic ions (exception made for certain chelating agents). Some ions are essential, some are beneficial while still others may be toxic elements. The fact that plants need ions but the solution is made up of dissociated salts, imposes the major constraint upon nutrient solutions, namely the balance of charge: the sum of the cation equivalents must be equal to the sum of the anion equivalents. This constraint is the major reason for the impossibility of using classical experimental designs (factorial-type designs) with nutrient solutions and the main argument for defining nutrient solutions as 'mixture' systems, because it is easily understood that the ionic balance constraint equals the mixture constraint (Eq. 1 and 2). Moreover dissociation, precipitation and complexation reactions further reduce the region of chemical feasibility. These additional constraints define the factor space as a 'constrained mixture' system (Eq. 3 and/or 4). Furthermore, the total ionic strength can be considered as a process variable. Thus the problem of experimentation with nutrient solutions in plant nutrition can be dealt with by using the theory of mixture designs and model forms.

Results

In what follows two simplified examples are presented to illustrate the application of mixture and optimal design theory in hydroponic, plant nutritional research.

Example 1. A whole simplex design to investigate the effects of cation composition of the nutrient solution on the head production in hydroponic chicory forcing

Nutrient solutions were made up consisting of each of the three cations K^+, Ca^{++} and Mg^{++} individually and combined. A six-point simplex

Table 1. The matrix of the design points (proportions), the mean and standard error of the mean for the head weight (*g*) for Example 1

Point	K^+	Ca^{++}	Mg^{++}		Mean	Std err
1	1	0	0		128.1	6.2
2	0	1	0	Vertices	119.5	6.6
3	0	0	1		97.1	5.8
4	0	0.5	0.5		131.2	7.1
5	0.5	0	0.5	Edge	136.5	6.8
6	0.5	0.5	0	centroids	120.3	7.0
7	0.33	0.33	0.33	Overall centroid	135.4	8.1

lattice design (points 1 to 6, Table 1) in the cation space (K^+, Ca^{++}, Mg^{++}), combined with an average composition of anions (0.33 NO_3^-, 0.33 $H_2PO_4^-$ and 0.33 SO_4^{--}), was set up to screen the effects of the different cations over the whole cation simplex. The six-point design was extended with the overall centroid (point 7, Table 1) as a check-point for testing goodness of fit of the proposed second-order model. The design consisting of points 1 to 6 is D-optimal with respect to a second order Scheffé canonical model. The design points are shown in Figure 1.

25 cut roots were assigned to each treatment solution and forced. At harvest, production and quality parameters were measured per root. The average head weights (*g*) and the standard deviation of the mean of the 25 roots per solution are listed in Table 1.

The model was fitted to the data where the cations are expressed as proportions of half the total ionic strength, which was 50 mval L^{-1}.

The regression equation for the second order model of the yield (FW) as a function of the cation composition is:

$$FW = 128.0*K^+ + 119.4*Ca^{++} + 97.0*Mg^{++} - 12.2*K^+*Ca^{++} + 97.4*K^+*Mg^{++} + 93.3*Ca^{++}*Mg^{++}$$

with $R^2 = 0.995$ and $R_A = 0.992$. The estimated head fresh weight surface, generated from the model, is plotted in Figure 2.

Significance tests were performed on the coefficient estimates of the nonlinear blending (crossproducts) terms in the fitted model to determine if the head fresh weight of the 50:50 blends of the cations differed from the average of the head fresh weights corresponding to the single cation solutions. All three estimates (−12.0, 97.6 and 93.2) were significantly different from zero ($p < 0.01$). Based on the signs of the coefficient estimates, head fresh weights of the two cation blends with Mg^{++} were significantly higher, meaning Mg^{++} blended synergistically with K^+ and Ca^{++}. The average head fresh weights of the binary blend of K^+ and Ca^{++} was significantly lower than expected from additive blending of K^+ and Ca^{++}. These nonlinear blending characteristics of the two-cation blends are reflected in the nonplanar shape of the

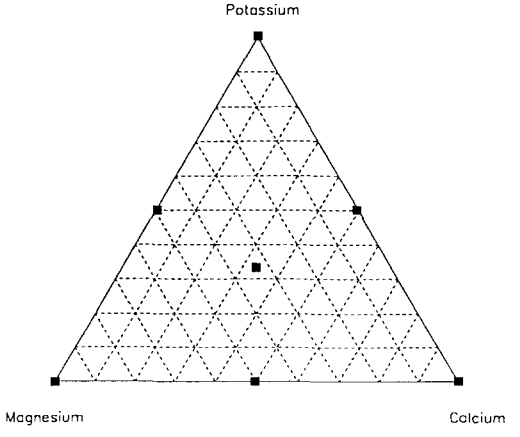

Fig. 1. A six point simplex-lattice design in the cation factorspace, with the overall centroid as a checkpoint.

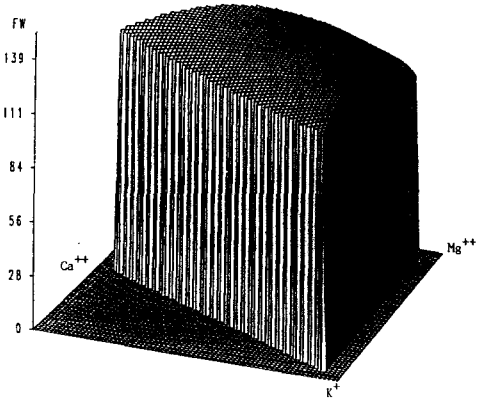

Fig. 2. The FW of chicory heads in function of cation composition.

estimated head fresh weight response surface that is plotted in Figure 2. Although generally not tested, the coefficient estimates (128.0, 119.4 and 97.0) of the linear blending terms in the model represent average head fresh weights of solutions containing only K^+, Ca^{++} or Mg^{++}, respectively.

The shape of the surface can be further explored:

— by calculating the expected response functions along different axes of the cation space
— by locating the stationary point by canonical analysis of the response surface
— by the evaluation of slope functions.

Component interaction effects can be evaluated:

— by comparing the estimated response value at points of interest with the estimated response at a reference mixture
— by computing total and partial effects.

As a result of the analysis performed, this response surface, along with the corresponding fitted model above, provides an accurate description of the process under study, emphasizing the multivariate interactional (linear and nonlinear blending) nature of plant nutritional problems.

Example 2. A constrained mixture design to explore the optimal zone of cation composition of the nutrient solution for growth and development of tomato

To study the effects of potassium, calcium and magnesium and their interaction, an experimental design is set up in the vicinity of the actual operating conditions for tomato, namely the cation composition of the standard solution of the Research Center for Soilless Cultures (point 13 of Table 2). The main question is 'How much deviation from the standard cation composition of the nutrient solution is allowed without sacrificing the growth and development characteristics of tomato plants?'.

For each ion a lower bound of 50% less and an upper bound of 50% more was considered possible, resulting in the following constrained experimental region. Cations are expressed in proportions of half the total ionic strength of the nutrient solution (80 mval L^{-1}).

Table 2. The matrix of the candidate points for Example 2

Point	K^+	Ca^{++}	Mg^{++}	
1	0.66	0.22	0.12	
2	0.22	0.66	0.12	
3	0.60	0.22	0.18	Extreme
4	0.66	0.28	0.06	vertices
5	0.28	0.66	0.06	
6	0.22	0.60	0.18	
7	0.41	0.41	0.18	
8	0.47	0.47	0.06	
9	0.63	0.22	0.15	Edge
10	0.66	0.25	0.09	centroids
11	0.22	0.63	0.15	
12	0.25	0.66	0.09	
13	0.44	0.44	0.12	Overall centroid

$$0.22 \leq K^+ \leq 0.66 \quad (5)$$

$$0.22 \leq Ca^{++} \leq 0.66 \quad (6)$$

$$0.66 \leq Mg^{++} \leq 0.18 \quad (7)$$

Applying the XVERT algorithm to the constraints above produced a region with six extreme vertices from which six edge centroids and an overall centroid point were generated. The matrix of the candidate points is shown in Table 2. The candidate list is plotted in Figure 3.

Out of these candidate points an 'optimal' design has to be selected. For this purpose, a model must be specified. Within this region it is assumed that the response can be approximated

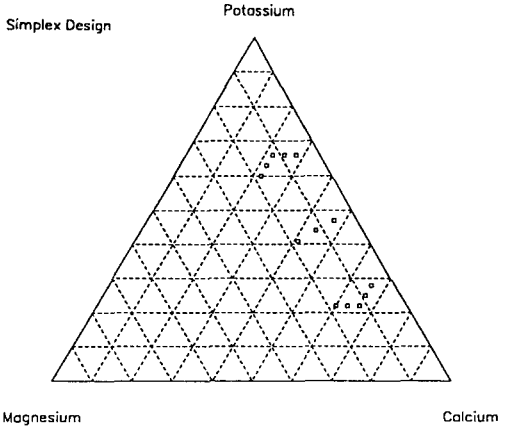

Fig. 3. The list of candidate points, consisting of the vertices, the edge centroids and the overall centroid.

reasonably well by a second-order Scheffé model which consisted of six terms. In the next step a D-optimal design is searched for with the use of Welch's branch-and-bound optimization algorithm. The number of design points necessary for supporting the fit of the quadratic model is six but it is recommended that at least two or three additional points be selected in order to cover the experimental region better than would be the case with the minimum number. The results are listed in Table 3.

The nine point design, consisting of the vertices, the centroids of the two longest edges of the polyhedron and the overall centroid was chosen. This nine-point design actually had a lower D-optimality value than all the other designs ranging in size from six to eleven points.

The experiment was carried out with these nine nutrient compositions. Per treatment destructive growth analysis was carried out on ten plants. The effects on the total leaf biomass (FW in *g*) are reported here (Table 4). First of all a quadratic canonical polynomial was fitted to the data. The statistical tests of the model parameters showed that the nonlinear blending estimates were not significantly different from zero, so they were dropped from the model resulting in the following linear blending model:

$$FW = 102.8*K^{+} + 109.2*Ca^{++} + 107.3*Mg^{++}$$

with $R^2 = 0.982$ and $R_A = 0.980$. The statistical evaluation of this model showed in an objective way that the response did not change with different cation composition within the region of interest. Thus Equations 5 to 7 give a first approximation of the zone of optimal response for the leaf weight. The response surface is shown in Figure 4. Of course, before claiming the zone as defined in equations 5, 6 and 7 as being optimal, other dependent variables or tomato plant characteristics, like production and quality, need to be investigated.

Table 3. The D-optimality criterion of designs with different numbers of treatments for Example 2[a]

Number of points	D-optimality criterion	Design consisting of point numbers
6	132.5	1 3 4 5 6 13
7	126.5	1 2 3 4 5 6 13
8	125.5	1 2 3 4 5 6 7 13
8	125.5	1 2 3 4 5 6 8 13
9	125.4	1 2 3 4 5 6 7 8 13
10	126.6	1 2 3(2) 4 5 6 7 8 13
10	126.6	1 2 3 4(2) 5 6 7 8 13
11	126.6	1 2 3 4(2) 5 6(2) 7 8 13
11	126.6	1 2 3 4(2) 5(2) 6 7 8 13

[a] Numbers between parenthesis indicate replication of that particular point.

Table 4. The matrix of the design points (proportions), the mean and the standard error of the mean for the total leaf weight (*g*) for Example 2

Point	K^+	Ca^{++}	Mg^{++}	Mean	Std err
1	0.66	0.22	0.12	97.3	9.8
2	0.22	0.66	0.12	106.1	6.5
3	0.60	0.22	0.18	110.4	6.0
4	0.66	0.28	0.06	109.5	4.7
5	0.28	0.66	0.06	109.2	6.5
6	0.22	0.60	0.18	108.6	6.2
7	0.41	0.41	0.18	107.1	6.6
8	0.47	0.47	0.06	105.3	6.9
13	0.44	0.44	0.12	102.3	7.5

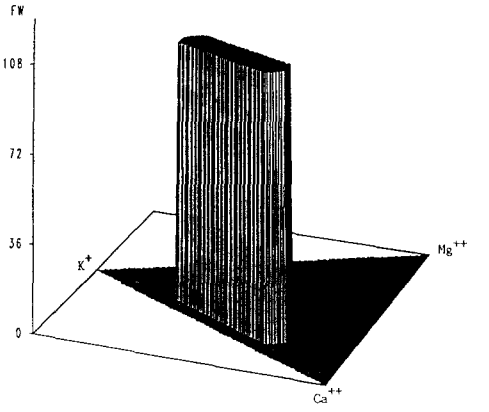

Fig. 4. Total leaf weight (*g*) of tomato in function of cation composition over an irregular shaped experimental region.

Conclusion

The application of mixture theory in terms of mixture designs and model forms is an indispensable tool for investigating nutrient solutions in hydroponic plant nutritional research.

In the optimization of nutrient solution composition, the emphasis is placed on multivariate investigation of the zone of optimal response as a function of the ion composition and the total ionic strength of the solution. This multivariate approach makes the study of ion interaction effects on well defined response variables possible. This work is a valuable tool in mineral nutritional research, because for the first time the chemical feasibility conditions of such solution, combined with additional chemical, physiological or economical constraints, form the foundation of the statistical experimental design theory, which makes the optimization of complex mixtures of ions in relation to response variables possible.

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