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PLOTTRIANGLE, A COMPUTER PROGRAM TO PLOT DIAGRAMS OF THREE- AND FOUR-COMPONENT MIXTURES

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SUMMARY

In many experiments on the development of detergent products mixtures are involved in which the ratio of the components is varied. The results of such experiments can be visualised by plotting the response function. A computer program (PLOTTRIANGLE) has been written for the Calcomp graph plotter to plot contours of arbitrary response functions in three- and four-component systems. The theory underlying this program is described and its effect on various (test) functions is shown. Using a transformation and the computer program PLOTTRIANGLE, the program PLOTRECTANGLE was written to plot the contours of an arbitrary function of two variables. Both programs have been written in Fortran IV (G-level) and make use of the standard COMPLOT utility plotting subroutine package.

1. INTRODUCTION

A mixture experiment is an experiment in which the response is a function only of the proportions of the components present in the mixture and not a function of the total amount of the mixture (Cornell 1973). The components in an experiment are the chemical compounds (or mixtures of compounds) necessary to make all relevant compositions in the experiment. This is the technical definition of a mixture experiment that raises the question why we should use proportions as the "independent" variables to describe a response

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surface. We can even go back further and pose the question why we are fitting. In this context, we quote from the discussion in Nelder (1966): "The choice of function for the fitting of a response surface raises a general question - why are we doing the fitting at all? Sometimes, it is hard to see any more justification than that the writer wishes to give an air of respectability to his data. Needless to say, an ill-fitting surface is no compliment to an accurate set of data, and it is adding insult to injury when such a surface is justified, as sometimes happens, by the quotation of an $\underline{R^2}$ value, which can be useless as an indicator of goodness of fit. (One need go no further than the well-known example $\underline{y} = \underline{x^2}$, $\underline{x} = 1(1)n$, for which the straight line fit has an $\underline{R^2}$ exceeding 0.93). With more justification, the analyser may claim that the fitted surface sums up the data in relatively few quantities (the parameter estimates and perhaps a measure of error), and allows for interpolation where required. Subject to the proviso that the surface used really does fit, so far as can be established from the data, this is fair enough. It is when we come to consider the combination of data that doubts begin to arise about the use of some arbitrary standard form of surface, such as ordinary polynomials. For if we are to 'make sense' of several sets of data and each set is summed up by a set of parameter estimates, then we must search for some pattern in these sets of estimates."

We consider response surface fitting merely as an alternative for tables to describe experimental data. By taking the proportions as the "independent" variables, these variables are scaled equally. Further, the model should be chosen such that a sufficiently accurate description of the experimental data is possible. Sometimes, physical chemistry gives a theoretical relationship between the independent variables and the response. In most practical situations, however, it is impossible or it will require too much effort or time to derive such a relationship. Ordinary polynomials may be sufficient in most such cases, while alternative models as proposed by Becker (1968) can also be tried. John and Quenouille (1977, chapter 9) gave an excellent survey of experiments with mixtures while most literature on this subject can be found in Cornell (1979). The computer program described in this article may help the experimenter in presenting his data from well-designed mixture experiments. Hopefully, it will not be misused as a gum to glue experimental data which are gathered in some unsystematic way from data banks or other doubtful resources.

2. THEORY AND NOTATION

We will represent the proportion of the i-th component X_i in a k-component mixture by x_i, so

$$x_i \geqq 0, \quad i = 1(1)k$$

and

$$\sum_{i=1}^{k} x_i = 1 \text{ (or 100\%)} \qquad [1]$$

x_i may be either a mol or a weight fraction, but not a volume fraction because volume fractions are generally not additive. In this article, we will use percentages instead of proportions.

On the basis of Eq. [1], the experimental space of a k-component mixture has the dimension (k-1). So the "independent" variables x_i ("independent" in the sense of "describing" as is usual in regression) are linearly dependent. The response function in a k-mixture design is a function of $x_1, \ldots, x_k$, thus

$$\text{response} = f(x_1, \ldots, x_k)$$

Scheffé (1958) has developed models for mixtures which are given in Gorman and Hinman (1962). Later, Becker (1968) proposed alternative models with additive properties which may be more suitable for certain cases.
The experimental space of a three-component mixture is drawn in Fig. 1.

For a three-component system, we can plot contours of f above the experimental plane from Fig. 1. For example, the contours of heights 4,000 (1,000) 9,000 of the function $f = x_1^2 + x_2^2 + x_3^2$ are the circles shown in Fig. 2.

The coordinates of an arbitrary point (x_1, x_2, x_3) in Fig. 2 are found by projection parallel to the sides of the triangle as shown in Fig. 3; so the length of each side is 100%.

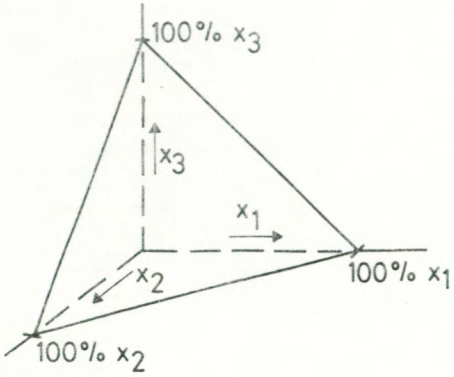


Fig. 1 The experimental space of a three-component mixture.

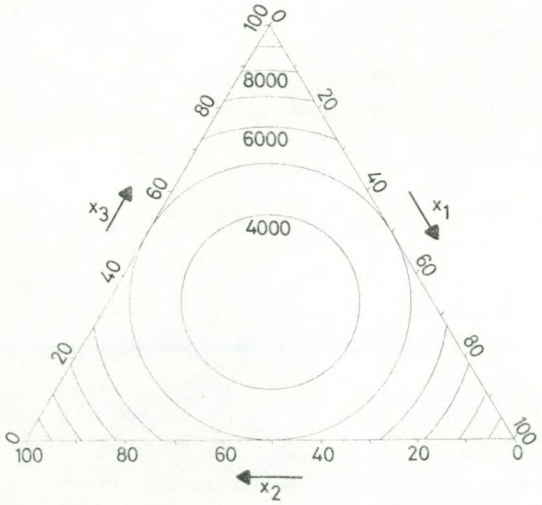


Fig. 2 Contours of heights 4,000 (1,000) 9,000 of $f = x_1^2 + x_2^2 + x_3^2$.

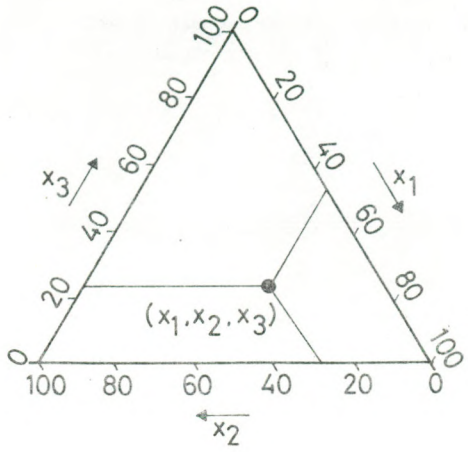


Fig. 3 Determination of coordinates of (x_1, x_2, x_3) by parallel projection.

The perpendiculars of the triangle are called "the axes", see Fig. 4.

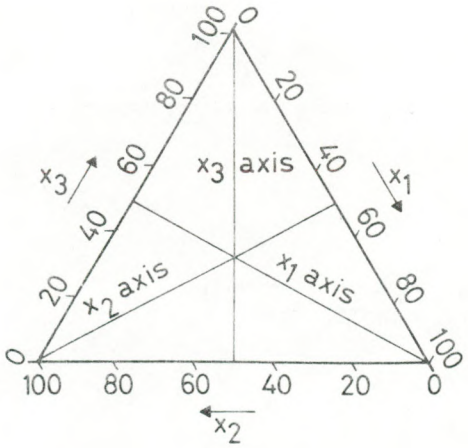


Fig. 4 Axes of the triangle.

A different way, used in physical chemistry, to find the coordinates of a point (x_1, x_2, x_3) is by perpendicular projection on the sides as shown in Fig. 5; so the length of each axis is 100%.

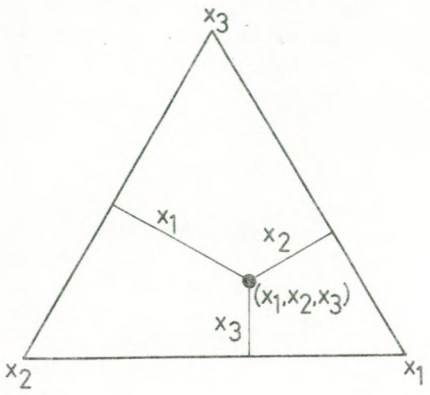


Fig. 5 Determination of (x_1,x_2,x_3) by perpendicular projection.

Contours which lie entirely within the triangle are called "closed contours"; the others will be called "open contours". As we can see from Fig. 2 there may be several open contours for the same height, all with starting/end points on the sides of the triangle.

In a four-component mixture, the experimental space can be represented by the tetrahedron of Fig. 6.

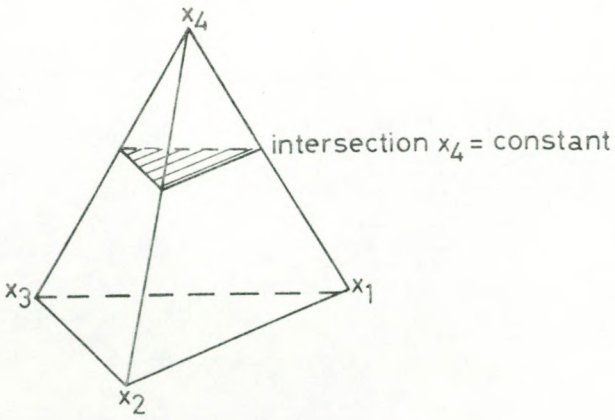


Fig. 6 Representation of experimental space in a four-component mixture.

Contours of the response function of a four-component mixture can be plotted by intersection of the tetrahedron and plotting contours of each slice.

The computer program PLOTTRIANGLE can plot contours of an arbitrary function of three- and four-component mixtures. The limitations are that for each height, only one closed contour (with highest value x_3) is plotted if there are no open contour(s) of this height and that in the four-component case, intersections are only possible of the planes x_4 = 0(10)90%. If necessary, these limitations may be avoided by transformation(s) of the components into "pseudo-components" as is done in section 6.

3. METHOD TO FIND A CONTOUR

The principle of the simplex method is used to draw the contours of a response function. This simplex method, described in Adby and Dempster (1974, chapter 3.2), is designed to find the optimum of a function of two (or more) variables by folding down a triangle. Because the experimental area is triangular, it can be ideally subdivided into a network of smaller triangles. For a three-component mixture, the triangle (experimental space) is subdivided into (1 + 3 + 5 + ... + 199) = 10,000 subtriangles with sides of 1% as shown in Fig. 7.

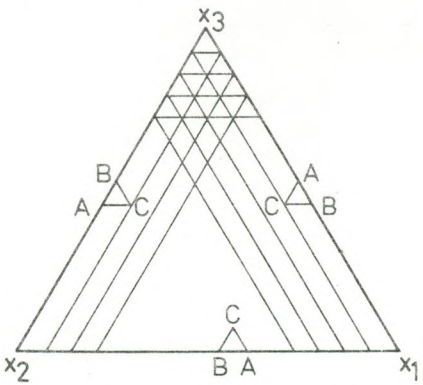


Fig. 7 Subdivision of experimental space for a three-component mixture.

To find the contour(s) of some chosen height h, the next procedure is followed:

a) consider all 297 subtriangles along the three sides of the triangle;
b) select the subtriangles ABC with h between f(A) and f(B); these subtriangles contain a starting/end-point for an open contour of height h. The orientation of A, B and C is always clockwise, taking AB as the side we start from and moving in the direction of C (see Fig. 7);
c) the starting/end-points are found by linear interpolation between A and B;
d) in the first start triangle, we look whether the contour passes through AC or BC. This side becomes AB from the next subtriangle and we calculate the new point C;
e) continuing in this way, we will end at a different starting/end-point (Fig. 8), which is scratched as starting point;
f) start with the next starting/end-point which is not scratched at e);

In this way, we will find all open contours for height h. Because of the practical considerations that open as well as closed contours for height h will hardly occur at the same time and that the admission of this case will require much more computer time and memory capacity, we only look for a closed contour for height h if no starting point for an open contour has been found. So, if no starting point of an open contour is found, one of a closed contour is looked for by searching the sides $x_3 = 99(-1)1$ of the downwards directed subtriangles.

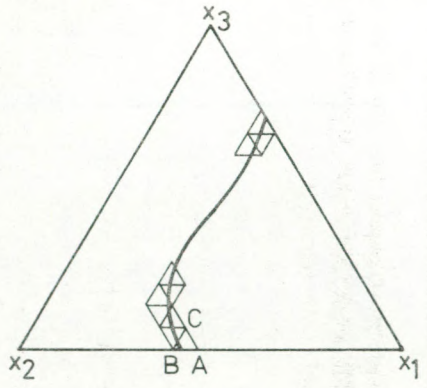


Fig. 8 Method to find an open contour.

Special provisions must be made if a starting/end-point lies on a edge-point (A or B) or when the contour passes through C. In both cases, we look for a continuing point on the three triangles surrounding this point in the search direction (Fig. 9).

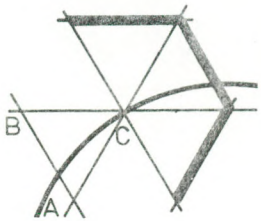


Fig. 9 Continuation if a contour passes through an edgepoint.

For a four-component mixture, it is possible to plot the intersections of the multiple-of-10% planes for the fourth component. To get an impression of the response in this case, one can reconstruct the tetrahedron, e.g. by drawing the plots on equidistant transparent sheets.

4. TEST OF THE PROGRAM WITH EXAMPLES OF DIFFERENT RESPONSE FUNCTIONS

The program is tested for several theoretical functions, which may cause difficulties or show the limitations of the program. These are plotted to give also an impression of the kind of response surfaces that are generated by the different functions.

The function in Fig. 10 is constant (100) within the inner triangle and the contours are parallel to the sides. For even values of h, the contours lie on the sides of the subtriangles (pass through C). If the starting/end-points of the contour of height 100 are scratched as a starting point, only part of this triangle will be drawn. To overcome this difficulty, the starting/ end-points are not scratched if they are the edge-point of a subtriangle. (Check that tangents will only be drawn in these points). As a consequence, open contours with starting point as well as end-point on the edge of a subtriangle are drawn twice.

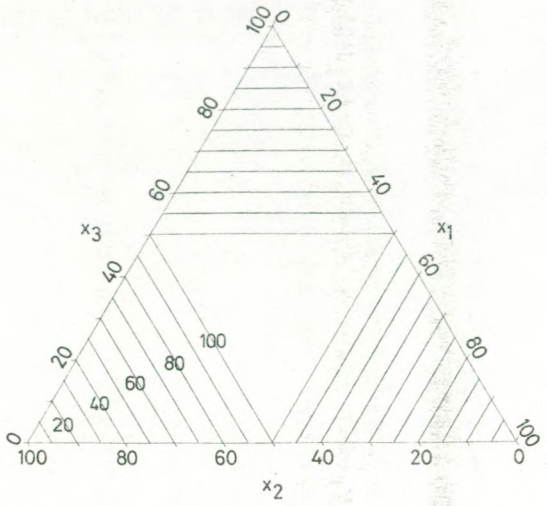


Fig. 10 $f = \min(x_1, 100 - x_1) + \min(x_2, 100 - x_2) + \min(x_3, 100 - x_3)$; $h = 0(10)100$.

The contours of the function shown in Fig. 11 are closed and identical to the base triangle. The edges are sharp if h is integer and otherwise rounded. Special provisions have been made in the program to handle the sharp edges and to start if h is integer.

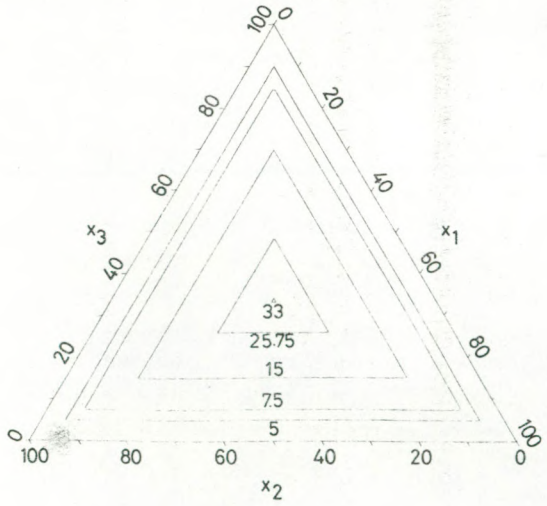


Fig. 11 $f = \min(x_1, x_2, x_3)$; $h = 5, 7.5, 15, 25.75, 33$.

The function in Fig. 12 shows the limitations of the program. For values of $h < 1$, the correct contours are not found because the subdivision in sub-triangles of 1% is too crude.

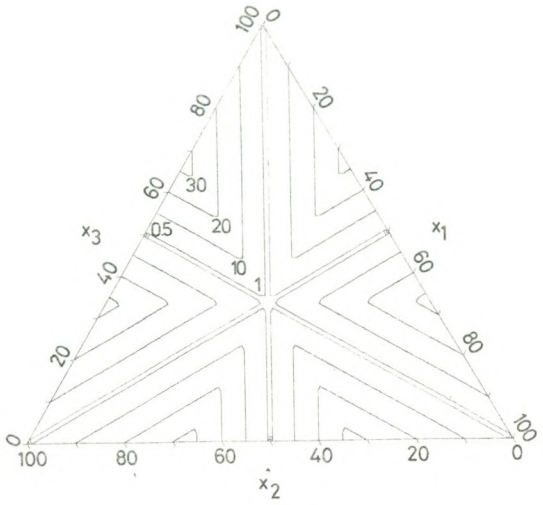


Fig. 12 $f = \min(|x_1-x_2|, |x_1-x_3|, |x_2-x_3|)$; $h = 0.5, 1, 10, 20, 30$.

The contours of height 0 shown in Fig. 13 are the lines $x_i = 100/3$ which pass through the saddle point (100/3, 100/3, 100/3). In the neighbourhood of this saddle point, the contours are not drawn exactly.

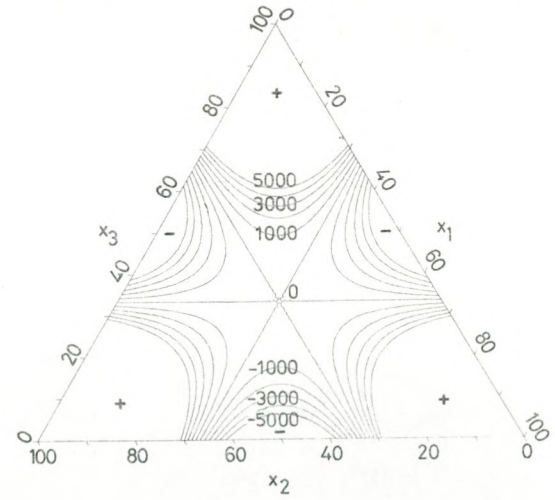


Fig. 13 $f = (x_1-100/3)(x_2-100/3)(x_3-100/3)$; $h = -5000(1000)5000$.

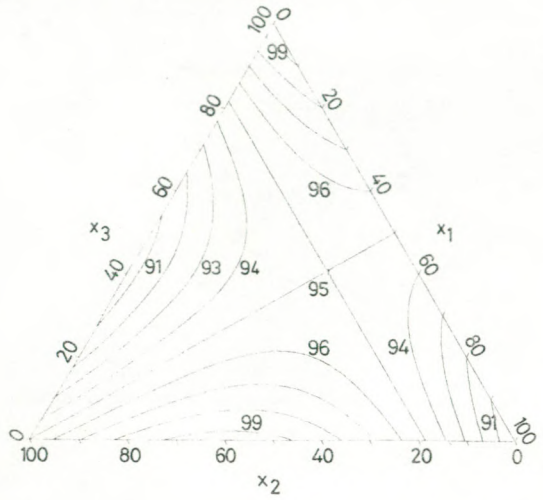


Fig. 14 $f = x_1 + 0.95\,x_2 + 0.9\,x_3 + 0.0027\,x_1x_2 + 0.0027\,x_2x_3$; $h = 90(1)100$.

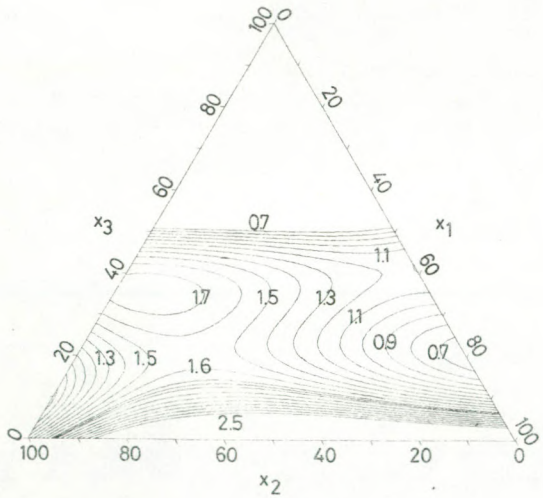


Fig. 15 $f = 0.03376\,x_1 + 0.0116\,x_2 - 0.3773\,x_3 + 0.0006628\,x_1x_2 + 0.007202\,x_1x_3 + 0.007638\,x_2x_3 - 0.0001263\,x_1x_2x_3 - 0.000003367\,x_1x_2\,(x_1-x_2) - 0.00006295\,x_1x_3\,(x_1-x_3) - 0.0000468\,x_2x_3\,(x_2-x_3)$; $h = 0.7(0.1)2.5$ and 1.75

In an example, derived from Gorman and Hinman (1962), the contour of height 95 starts in the edge-point (0,100,0) and passes through a saddle point (Fig. 14).

Fig. 15 shows a function to simulate wood grains. The closed contour of height 1.75 is not drawn because there is an open contour of the same height.

5. EXAMPLE OF A FOUR-COMPONENT DETERGENT MIXTURE

The experimental area is the bounded region in the four-component system drawn in Fig. 16.

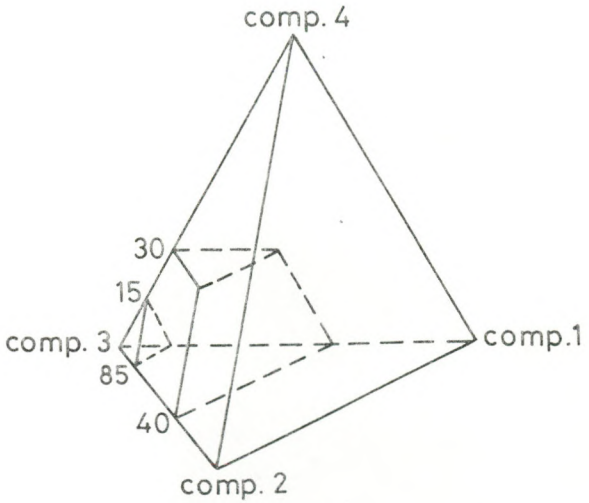


Fig. 16 Representation of experimental area in a four-component system

The bounds are 40% ≤ component 3 ≤ 85% and component 4 ≤ 30%. The mean detergency of six replicates (in blocks) for 32 points within this experimental region is given in Table 1.

Table 1 Mean detergency ($\bar{D}$) of six replicates

Components				
1	2	3	4	$\bar{D}$
60	0	40	0	12.60
45	15	40	0	15.42
30	30	40	0	12.82
15	45	40	0	14.78
0	60	40	0	15.13
45	0	55	0	12.83
30	15	55	0	12.83
15	30	55	0	13.23
0	45	55	0	11.20
30	0	70	0	13.82
15	15	70	0	11.10
0	30	70	0	8.94
15	0	85	0	10.10
0	15	85	0	6.62
45	0	40	15	15.73
30	15	40	15	15.80
15	30	40	15	18.00
0	45	40	15	17.95
30	0	55	15	15.17
15	15	55	15	14.72
15	15	55	15	15.26
15	15	55	15	15.80
0	30	55	15	14.02
15	0	70	15	15.58
0	15	70	15	13.03
0	0	85	15	4.65
30	0	40	30	18.92
15	15	40	30	19.38
0	30	40	30	18.33
15	0	55	30	17.88
0	15	55	30	15.35
0	0	70	30	7.30

The mean detergency for each point has a standard error of s = 1.0.

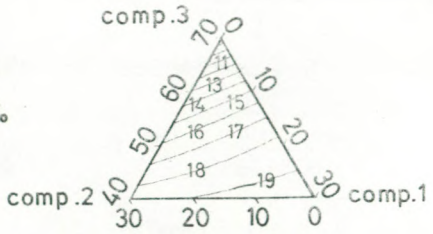
Sequential fitting of a linear, quadratic, restricted-cubic and cubic polynomial gives the analysis of variance.

	df	SS	MS
Linear	3	265	88.3
Quadratic	6	80	13.3
Restricted-cubic	4	18	4.5
Cubic	6	12	2.0
Lack of fit	12	16	1.3
Total	31	391	
Error	147	160	1.0

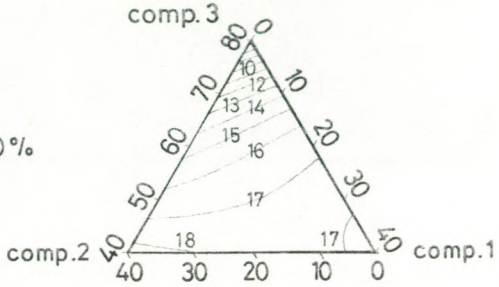
With x_1 = % component 1, x_2 = % component 2, x_3 = % component 3 and x_4 = % component 4, the fitted cubic polynomial is shown in Fig. 17. The term $x_3x_4\,(x_3-x_4)$ is not present in the model because it depends linearly on the other 19 terms. Fig. 17 shows contours of the intersections component 4 = 0, 10, 20 and 30%. To avoid extrapolation only the interior of the experimental area has been drawn.

Fig. 17 $f = 0.6421\,x_1 + 0.744\,x_2 - 0.0308\,x_3 - 0.3862\,x_4 - 0.001405\,x_1x_2 - 0.007265\,x_1x_3 + 0.009982\,x_1x_4 - 0.009504\,x_2x_3 + 0.008612\,x_2x_4 + 0.01036\,x_3x_4 - 0.0002093\,x_1x_2x_3 - 0.000299\,x_1x_2x_4 - 0.00003999\,x_1x_3x_4 - 0.00002481\,x_2x_3x_4 + 0.00001983\,x_1x_2(x_1 - x_2) - 0.0001403\,x_1x_3(x_1 - x_3) - 0.0002205\,x_1x_4(x_1 - x_4) - 0.0001107\,x_2x_3(x_2 - x_3) - 0.00009661\,x_2x_4(x_2 - x_4)$;
$h = 7(1)19$

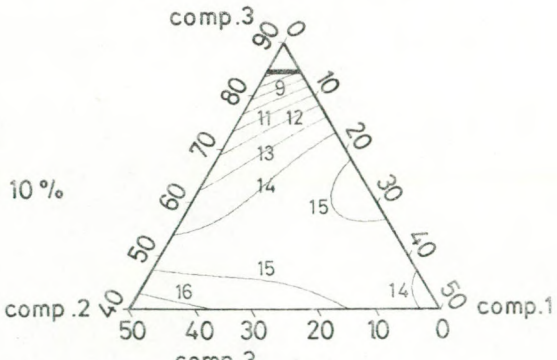
comp. 4 30 %



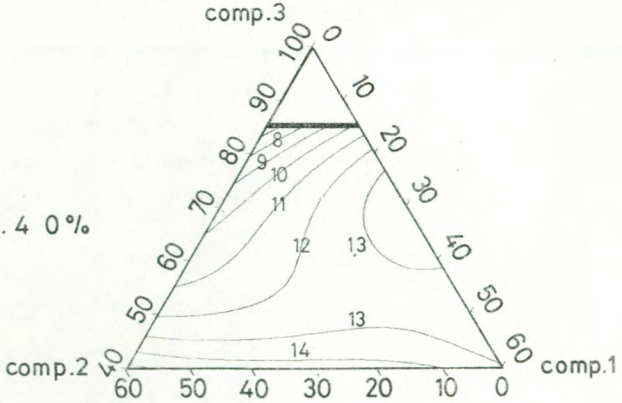
comp. 4 20 %



comp. 4 10 %



comp. 4 0 %



6. SUGGESTIONS USING PLOTTRIANGLE

A computer program to plot contours will often be used for the presentation of experimental results. The validity of a plot fully depends on the quality of the experimental data and the goodness-of-fit of the model to these data. Generally, the experimenter will take his experimental points equally divided over the region of interest. This may be the whole triangle or tetrahedron, but also parts of it. More points should be chosen in "difficult" regions, e.g. in regions where the response is expected to bend sharply possibly due to boundary effects.

If a physical relationship between the response and the proportions is known, the analytical function describing this relationship will generate the response surface. Our practice, however, shows that in most cases, the experimenter cannot provide us with the relevant physical relationship. A linear or quadratic polynomial may describe the data satisfactorily in cases where the surface does not vary too much. However, one should be careful when applying these polynomials in the case of sharply bending or bounded surfaces (e.g. in the case of "saturation", see Nelder (1966)) and/or bounded accessible and relevant experimental regions (see Gorman and Hinman (1962)). Alternative models as proposed by Becker (1968) may be more appropriate to handle these cases.

A necessary condition to get the correct impression of the shape of the response surface is to plot contours at equidistant values of the response function and not at selected values which result in equidistant contours in the diagram. As mentioned before, extrapolation outside the experimental area should be avoided. In this case of a bounded experimental region one can try to enlarge the plot by transformation. The same may help when plotting other than multiple-of-ten slices for x_4. In the example of section 5 the experimental area is bounded by $40 \leq x_3 \leq 85$. By the transformation

$$x_1' = x_1 * 100/60 \qquad 0 \leq x_1' \leq 100$$

$$x_2' = x_2 * 100/60 \qquad 0 \leq x_2' \leq 100$$

$$x_3' = (x_3 - 40) * 100/60 \qquad 0 \leq x_3' \leq 75$$

$$x_4' = x_4 * 100/60 \qquad 0 \leq x_4' \leq 50$$

we enlarge this experimental area and are able to plot a more detailed picture of this area. Each lower bound can be handled in this way (see Kurotori (1966)), while other transformations can be found in Gorman (1970). If a contour of a certain height should cause difficulties in plotting, one might try a change of the last decimal(s) of this height.

7. PLOTRECTANGLE, A PRESENT BY TRANSFORMATION

Using a transformation and the computer program PLOTTRIANGLE, we have also written the computer program PLOTRECTANGLE to plot contours of an arbitrary function of two variables. Therefore we had to find a one-to-one transformation of a rectangle on the triangle which maps the sides of the rectangle on the sides of the triangle. For convenience, we take the coordinates y_1 and y_2 of the rectangle, also ranging from 0 to 100. So we have to find a one-to-one transformation T as represented in Fig. 18.

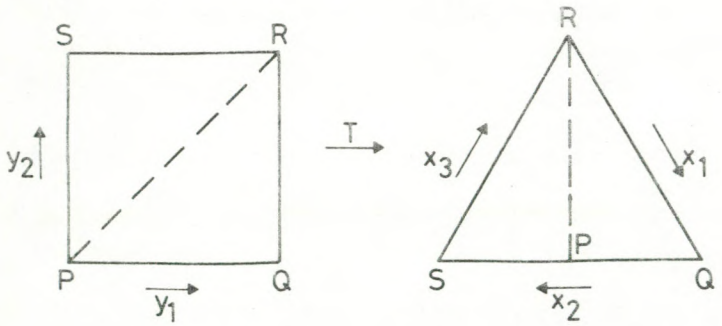


Fig. 18 Transformation T of a square on a triangle

The two dotted lines divide each figure into two symmetrical parts. It is obvious that a transformation T is sufficient, which represents the left upper part of the square on the left-hand side of the triangle and the right lower part of the square on the right-hand side of the triangle with the dotted lines on each other. Such a transformation T is given by

$$
\begin{aligned}
&\text{if } y_1 \geq y_2 \text{ (right lower part of the square):}\\
T\quad &(y_1,y_2) \to (50 + y_1/2 - y_2,\ 50 - y_1/2,\ y_2)\\
&\text{if } y_1 < y_2 \text{ (left upper part of the square)}\\
&(y_1,y_2) \to (50 - y_2/2,\ 50 + y_2/2 - y_1, y_1)
\end{aligned}
$$

with back transformation T^{-1}:

T^{-1} if $x_1 \leq x_2$ (left-hand side of the triangle):
$(x_1, x_2, x_3) \rightarrow (x_3,\ 100 - 2x_1)$
if $x_1 > x_2$ (right-hand side of the triangle):
$(x_1, x_2, x_3) \rightarrow (100 - 2x_2, x_3)$

The subdivision of the triangle from Fig. 7 is transformed by T^{-1} into the subdivision of the square from Fig. 19.

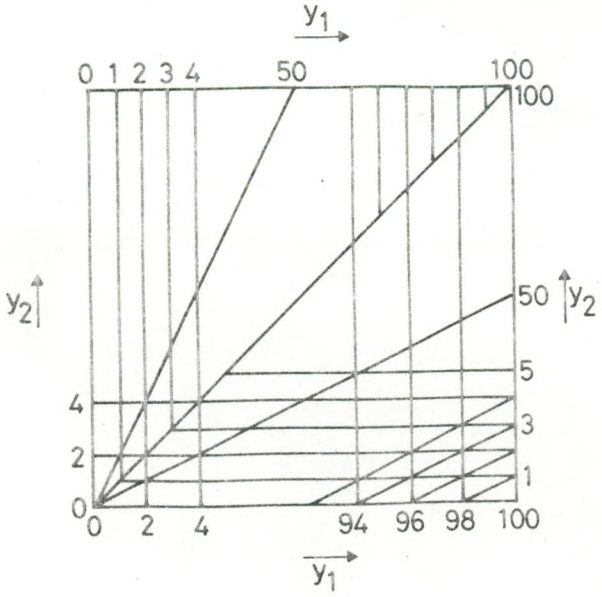


Fig. 19 Subdivision of the square after back-transformation T^{-1}

This subdivision of the square is sufficiently uniform to guarantee that the transformation T will produce smooth contours. For arbitrary plot length L_1 and L_2 of the y_1 and y_2 axes respectively, the subdivision of Fig. 19 is linearly transformed into the subdivision of Fig. 20.

The adequacy of this subdivision depends on the real (plotted) lengths L_1 and L_2, the ratio L_1/L_2 and the function to be plotted. If the ratio L_1/L_2 lies between 0.5 and 2 and the function has no narrow valley or mountain ridges, the subdivision of the rectangle (experimental space) will be sufficient to produce smooth contours in most practical cases.

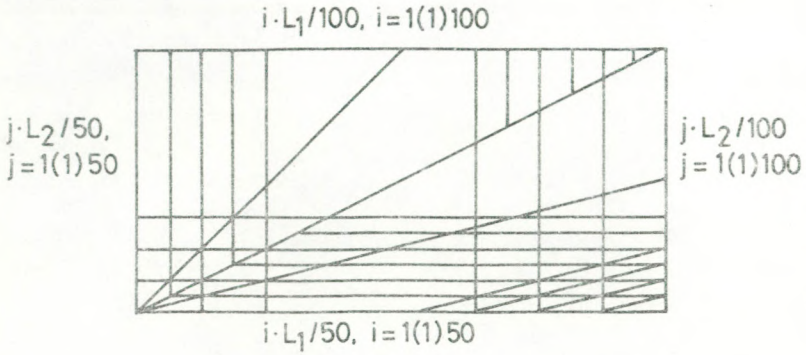


Fig. 20 Subdivision of the rectangle

The working of PLOTRECTANGLE is demonstrated by an experiment in which the detergency was measured from different compositions of two builders (Table 2).

Table 2 Mean detergency ($\bar{D}$) from ten replicates of 14 different compositions

Builder 1 (%)	Builder 2 (%)	$\bar{D}$
0	8.0	17.47
0	12.0	17.05
0	16.0	16.83
0	20.0	19.77
15.0	8.0	23.58
15.0	12.0	21.57
15.0	16.0	22.0
30.0	8.0	23.76
30.0	12.0	23.64
30.0	16.0	22.74
7.5	10.0	19.22
7.5	14.0	20.22
22.5	10.0	22.36
22.5	14.0	22.36

The standard error of these means was 0.6. Because the percentages of the two builders do not add up to the same amount for each composition, at least one more component must be varied. In this experiment, a filler was added up to a total of 53% in relation to the sum of the two builders and the filler. The remaining 47% was the same for all compositions. The experimental area can be drawn in a three-component diagram, for instance in the diagram builder 1 + builder 2 + filler = 50% shown in Fig. 21.

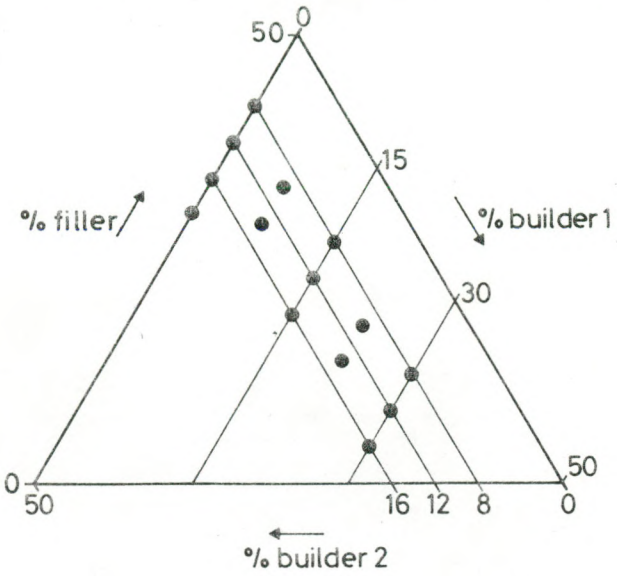


Fig. 21 Plot of the data from Table 2

In this picture, the experimental area is such a small part of the triangle that it was decided to switch to a rectangular system by ignoring the component filler. Fig. 22 is the plot of the means in the experimental area.

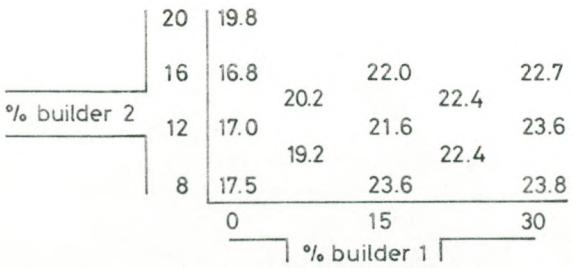


Fig. 22 Plot of the means from Table 2 in a rectangular system

One should be careful when representing a three-component system in a two-component one. If, for instance, all contour lines are horizontal, this suggests that only the second component determines the system properties. However, an increase of the second component by 1% is identical with a decrease of a third component by 1%, which could be equally responsible for the effect. Therefore, the plots do not go beyond visualising the situation and predicting optimum conditions. They do not allow any interpretation (relating the results to physical/ chemical phenomena). Moreover, suggested optimum conditions always have to be verified in an additional experiment. It is advised to omit only those components which do not influence the observed variable as e.g. filler in our case. Contours parallel to builder 1 + builder 2 = constant are in such a case "interpreted" as an influence of the varying total amount of builder only.

Successive fits of a linear, quadratic and cubic polynomial result in the quadratic model

$$\text{mean detergency} = 22.62 - 0.53x_1 - 1.081x_2 - 0.0067x_1x_2 - 0.0079x_1^2 + 0.0468x_2^2$$

in which x_1 = % builder 1 and x_2 = % builder 2. The contours of this function are given in Fig. 23 where only the interior of the experimental area has been drawn to avoid extrapolation.

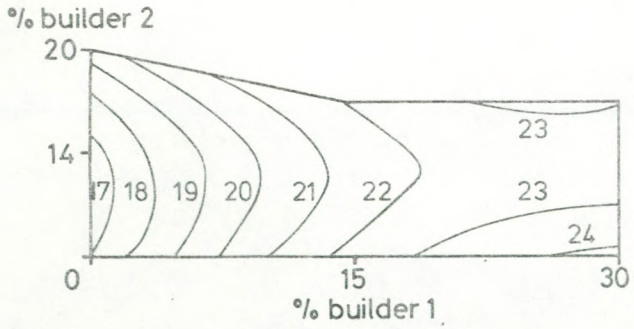


Fig. 23 Contours of the quadratic model for the data of Table 2

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Note. For details about the computer programs, please contact R. van Splunter.