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Experiments with Mixtures

Designs, Models, and the Analysis of Mixture Data

Second Edition

JOHN A. CORNELL

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Preface to the Second Edition

Since the publication of the first edition 9 years ago, approximately 35 papers have appeared in statistical literature that dealt with the construction of mixture designs and/or the discussion of methods for analyzing mixture data. Many of the paper topics had foundations set previously such as improved ways (algorithms) to generate designs for constrained mixture regions, alternative methods for measuring component effects in highly constrained mixture problems, and new designs and models for including process variables and/or the total amount of the mixture in these types of experiments.

As an active reviewer of papers as well as being an active participant in onsite seminars for various industries and short courses sponsored by the American Society for Quality Control, I have become increasingly aware of the types of mixture experiments that dominate the different areas of application, particularly industrial applications. Furthermore, during the past 22 years I have had the good fortune of working in an academic environment which has afforded the opportunity to fuel my research in a manner that blends theory with practice. As a result, this second edition contains a considerable amount of additional material, both new and not so new.

A new section in Chapter 1 compares a factorial experiment to a mixture experiment. Chapter 2 discusses the method of using check points for testing the adequacy of the fitted model, along with a numerical example which illustrates the technique. Rewriting the Scheffé-type mixture models by deleting one of the linear blending terms and inserting a constant term so that the model form conforms to the requirements of some of the more popular least squares model fitting programs is also included. Chapter 2 ends with questions that one might ask while planning to conduct a mixture experiment.

Chapter 3 once again addresses the use of independent variables with only slight changes. Additional comments regard the settings of the mixture components upon transforming from the design settings in the independent variables. A new formula is given for calculating the radius of the largest sphere, centered at the point of main interest, that will fit inside the simplex region. The four sections on the inclusion of process variables have been removed from Chapter 3 and placed in Chapter 7, which is now a chapter devoted entirely to the inclusion of process variables in mixture experiments.

The assigning of multiple constraints on the component proportions, Chapter 4, has experienced the greatest revision. Previously, only lower-bound pseudocomponents, now called *L*-pseudocomponents, were considered. In this edition, upper bound pseudocomponents, called *U*-pseudocomponents, are introduced and used for detecting inconsistent constraints. It is shown how the set of inconsistent constraints can be adjusted to make the set of lower and upper bounds consistent. A formula is given for enumerating the number of extreme vertices, edges, faces, and so on, of a constrained region based on the set of consistent constraints. This then leads to calculating the coordinates of the extreme vertices of the constrained region using *U*-pseudocomponents. A section on design strategy for fitting the Scheffé quadratic model over a constrained region has been added along with a section containing several examples of constrained mixture experiments. This section on examples of constrained mixture experiments aids users in checking the results obtained with their software packages, against those obtained by this author using the two programs, CONVRT and CONAEV, whose steps are now listed in Appendices A, B, and C of Chapter 10.

The analysis of mixture data, Chapter 5, now includes the plotting of the response trace for measuring changes in the response brought about by changing the proportion of a single component at-a-time. Chapter 6, on other mixture model forms, contains a new section on measuring additivity and interaction in the component blending properties by fitting log contrast models.

Chapters 7, 8, and 10 are new additions. Chapter 7 is devoted entirely to the inclusion of process variables and considers the total amount of the mixture as well. Combining lattice designs with factorial arrangements is taken from Chapters 3 and 5 of the first edition and is illustrated using the fish patty experiment previously found in Chapter 5. Testing the component blending properties and the effects of the process variables when one set of variables is embedded in the other set (mixture components embedded in the process variables and vice versa) is also illustrated. The use of fractional factorial designs in the process variables as well as fractionating the lattice designs in the mixture components through a computer-aided approach are two new sections. Designs and models for mixture-amount experiments close out Chapter 7.

Chapter 8 reviews orthogonal blocking strategies, comparing the estimates of the coefficients in the Scheffé models obtained using weighted and unweighted least squares formulas, the generation of optimal designs with the ACED-algorithm, and a technique that provides a prediction equation

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that possesses constant variance of prediction on concentric triangles for three-component systems. Reparameterizing the Scheffé-mixture models to models containing a constant term so that the terms can be centered and standardized is suggested as a remedy for improving the accuracy of the calculating formulas for the model coefficient estimates. Collinearity problems that arise from the fitting of Scheffé's models to data from highly constrained regions are also addressed. Chapter 8 ends with a method for fitting segmented Scheffé models to freezing point data that is collected from a binary system and exhibits a eutectic point. The method is illustrated with a numerical example.

Chapter 9 contains a review of matrix algebra, the method of least squares, and setting up an analysis of variance table. Chapter 10 is a collection of real data sets with partial solutions provided. The example data sets offer the reader an opportunity to work on problems with data sets that are larger in size than those provided in the exercises at the end of Chapters 2–8. An updated Bibliography contains more than 150 entries taken from the mixture literature and also recent related literature.

This expanded second edition is much more complete in its coverage of mixture designs and models particularly in the area of constrained mixture regions. Many of the new topics covered, particularly in Chapters 2 and 4, are important because most arose from questions that were asked during short-course discussions and plant visits. And while Chapters 2 and 4 are the lengthiest in terms of number of pages, in my opinion, they are the most important because they present designs and model fitting exercises for exploring the mixture surface *over the entire simplex region* and *over constrained subregions of the simplex*, respectively. As a classroom textbook for a one-semester graduate-level course, I would suggest Chapters 1–7 as basic material and then select from Chapters 8–10 according to need. If used as a reference or for self-study, Chapters 1–2 and 4–7 provide the necessary tools for dealing with almost any type of mixture problem.

In putting together the material for this second edition, I am indebted to many people. Heading the list of friends from industry are John Gorman who is now retired from AMOCO, Wendell Smith of Eastman Kodak Company, and Gregory Piepel of Battelle Pacific Northwest Laboratories. Others who attended the ASQC short courses on mixtures or who invited me to their particular companies to share a common interest in solving problems with mixtures are too numerous to mention here and to them I extend a heart warmed "thank you." I wish also to express my sincere appreciation to Ms. Pamela Somerville for her excellent typing.

JOHN A. CORNELL

Gainesville, Florida
April 1990

Preface to the First Edition

The primary purpose of this book is to present the fundamental concepts in the design and analysis of experiments with mixtures. The book focuses on the most frequently used statistical techniques and methods for designing, modeling, and analyzing mixture data, as claimed in the literature, and includes appropriate computing formulas and completely worked out examples of each method. Most of the mathematical examples were taken from real research situations.

The book is written for anyone who is engaged in planning or performing experiments with mixtures. In particular, research scientists and technicians in the chemical industries, whether or not trained in statistical methods, should benefit from the many examples that are chemical in nature. Several examples have been taken from research activities conducted in areas of food technology, while some examples were provided by research entomologists. Persons who are engaged in applied research in universities, principally from such departments as chemical engineering, chemistry, and statistics, as well as scientists in areas of agriculture such as food science, entomology, and nematology, should find the methods that are presented to be relevant and useful in their research. As a textbook on the subject of mixture experiments, the contents could serve quite nicely as a one-semester course in most applied curricula, or perhaps could supplement the coverage of a two-semester sequence of regression and response surface methodology.

Since this is the first edition, it has been necessary to exercise considerable selectivity in the choice of topics covered. Hence no claim is made that the coverage is exhaustive in either scope or depth. However, it is my feeling that the reader who works through the numerical examples in the middle five chapters (Chapters 2–6) and answers the questions listed at the end of these chapters will achieve a high level working knowledge of the tools that are used by most of the practitioners today who are involved in solving mixture problems.

The mathematical prerequisites have been kept to a minimum. Summation notation is used throughout and some background knowledge of the use of matrices is helpful. A review of matrix algebra is presented in Chapter 7 along with a discussion of the method of least squares for obtaining the parameter estimates in polynomial models. Chapter 7 could also serve as a refresher to readers who wish to review some of the fundamental ideas on the use of matrices in regression analysis. The matrix material has been placed at the end of the book so that the reader with an adequate knowledge of matrices may begin with the subject of mixture experiments in Chapter 1. Almost all of the computations throughout the book were performed on the APL system 360.

The first chapter introduces the subject of mixture experiments with several examples. Some general remarks on response surface methodology are made. An historical perspective of the relevant literature which presented most of the statistical research on mixture experiments is listed. Chapter 2 introduces the original mixture problem where the Scheffé lattice designs and associated polynomial models are applicable. Several numerical examples are provided that help to illustrate the fitting of the polynomial models to samples of mixture data that were collected at the points of the simplex-lattice and simplex-centroid designs.

In Chapter 3 a transformation is made from the system of the dependent mixture components to a system of independent variables. With the independent variables, standard regression procedures are suggested not only for the designing of the experimental runs but for the fitting of model forms as well. The idea of isolating the experimentation to a subregion of interest inside the simplex space where the region may be ellipsoidal or cuboidal in shape is also considered. Process variables, such as cooking time and cooking temperature in the preparation of fish patties, are introduced. Different types of model forms used to measure the influence the process variables could have on the blending characteristics of the components in mixture experiments are presented and discussed.

How the placing of additional constraints on the component proportions can affect the design configuration and the usual interpretation of the model parameters is considered in Chapter 4. Experimental design configurations for use in covering the restricted region of the simplex are mentioned, as are several types of polynomial model forms used for depicting the surface characteristics. Pseudocomponents are introduced, and the use of pseudocomponents rather than the original components is seen to simplify the steps in the design construction and the fitting of models when lower bound constraints are placed on the original component proportions. Some discussion on the design strategy when some or all of the component proportions are subjected to both upper and lower bound constraints is presented along with some suggested modifications that need to be made to interpret the model coefficients in these highly constrained problems. Grouping the components by categories is also studied.

Chapter 5 presents many techniques that are used in the analysis of mixture data. Testing the form of the fitted model, model reduction procedures, and the screening of unimportant components are just some of the topics covered. Investigating the shape characteristics of the surface by the measuring of the slopes of the surface along the component axes is discussed. Combining lattice designs in the mixture components with factorial arrangements of process variables as illustrated with data from a fish patty experiment in which patties that were made from three species of fish are prepared and processed by the three cooking and processing factors.

Alterations made to some of the terms of the Scheffé polynomials as well as the suggestion to use nonpolynomial models to model certain types of phenomena is the theme of Chapter six. Models that are homogeneous of degree one are shown to model additive component effects better than the polynomials. The use of ratios of the components as terms in the model is suggested particularly when relationships between the component proportions are more meaningful than the actual fraction of the mixture each component represents. Standard orthogonal designs, such as standard factorial arrangements, that can be used with independent variables are shown to be useful when working with ratios. Cox's polynomial, which is used for measuring the components effects, is compared with the several forms of Scheffé's polynomials. Two classes of octane-blending models are presented at the end of the chapter, and data are provided to help illustrate the numerical computations that are required to set up the prediction equations. Chapter 6 ends with a list of topics that were not covered here but which hopefully will be discussed in a future edition.

I am extremely grateful to many friends for their help in compiling the material for this work. In particular, I am indebted to Drs John W. Gorman and R. Lymann Ott, Professors Irving John Good (Virginia Polytechnic Institute and State University) and Andre I. Khuri (University of Florida), with whom I have had the pleasure of working on research problems in mixtures, and to Dr. Hubert M. Hill (Tennessee Eastman Company), who introduced me to the subject of mixture experiments in the middle 1960s. I am very much indebted also to Professor J. Stuart Hunter (Princeton University), who reviewed the initial drafts of this book; his many thoughtful and detailed comments on the style and content were instrumental in its organization. I wish to thank the many authors and various publishers for permission to reproduce their papers and tables and to thank the staff at John Wiley and Sons, particularly Beatrice Shube, for her encouragement in completing this work. Finally, I would like to express my sincere appreciation to Donna Alexander for her excellent typing of the final manuscript.

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Gainesville, Florida
August 1980

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