Agenda for Chemometricians

It is most appropriate that the proceedings of this conference are going to be dedicated to the memory of Jack Youden. He was interested in many of the topics that are being considered at this conference, for example, interlaboratory comparisons, calibration, analytical methods, and measurement errors—both systematic and random. He was indeed a pioneering chemometrician, before the name existed. He was also interested in explaining to chemists, chemical engineers, and others how they could benefit by using statistical methods.

I'm sure Youden would have been pleased with this conference, which provides a forum for chemists, statisticians, and others interested in chemometrics to discuss research of mutual interest. He also might have observed that chemometrics as a field has reached a level of maturity that warrants consideration of questions related to spreading the word to others, to non-chemometricians, so that they could take advantage of the techniques that are now available. In other words, perhaps chemometrics as discipline has reached a sufficiently advanced stage of research and development that questions of production should now be addressed. What are our most useful products? Who are out customers? Which products would they find most valuable? What are the obstacles that prevent these customers from using these products now? How can these obstacles be overcome? What are the most important things that can be done in the next three years to reach new customers? What should the agenda be for chemometricians in the next few years?

There are two ways to learn. One is to listen, as in a lecture. The other is to engage in a dialogue, as in a conversation. The first way is passive. The second is active. Let's try the second way to learn from one another how we might answer these questions.

[Participants at this point wrote out answers to these questions, discussed them, and voted on them. The top vote-getters for the most important things that can be done in the next three years to reach new customers were the following, listed in order of decreasing number votes:

1. Organize joint conferences with chemists.
2. Write textbooks on chemometrics.
3. Conduct workshops and teach short courses.
4. Write user-friendly software.
5. Teach chemometrics to graduate students.

6. Write tutorial, expository, and review articles.
7. Undertake joint research projects with chemists.
8. Publicize success stories.
9. Teach chemometrics to undergraduate students.
10. Communicate with management.
11. Hire professionals to help with a public relations effort.
12. Teach chemometrics to high school students.]

I recommend that we take action on the basis of this list. Let me now make a few observations in closing. I would like to suggest a different starting point for statistics courses. Let us represent the relationship between an observed response y and variables $x_1, x_2, \ldots$ as

$$y = f(x_1, x_2, x_3, x_4, x_5, \ldots, x_{126}, \ldots) .$$

Many, many, many variables affect y. It is the fluctuation of these variables that gives us different answers when we repeat an experiment two or more times under "identical conditions." We are often interested in creating a mathematical equation (model) that involves a subset of the variables. For purposes of illustration, suppose this subset is (x_1, x_2). We can then write

$$y = f(x_1, x_2) + g(x_1, x_2, x_3, x_4, x_5, \ldots, x_{126}, \ldots) .$$

Note that the g function includes x_1 and x_2 (because of lack of fit of the model) as well as all the other x's. Lack of fit occurs, for example, because the model f may be taken to be linear in x_1 and x_2 but the actual relationship may be nonlinear in x_1 and x_2. The function g is most often called experimental error, and it is almost as often endowed by writers with an abundance of desirable and well-known properties. They call it a random variable. A sequence of these experimental errors, they frequently say, can be assumed to be independent, identically distributed according to a Normal distribution with a zero mean and constant variance. I believe that statisticians too readily make this assumption and others like it. *Sometimes* such an assumption makes sense, sometimes not. We should be more careful on this point.

An adequate model is a function that will turn data into white noise, as George Box has said. An analogy that I find useful involves a process for separating gold particles from a slurry. If the process is fully efficient, the waste stream will contain no gold. It is therefore prudent to check the waste stream to see if it contains any gold. Likewise in creating and fitting models, it makes sense to examine residuals to see if they contain any information. The data contain information (that's the gold we want to get), and a good model will extract all the information in those data. Hence the residuals will be manifestations of white noise, an informationless sequence of values.

Chemists and chemical engineers could benefit from knowing more about variance components, statistical graphics, and quality control techniques (including Shewhart and cumulative sum charts). But, above all, I think they would find statistical experimental designs to be the most useful thing of all that chemometricians have to offer. Such designs provide a practical means for increasing research efficiency, which might be defined as the amount of information one obtains per dollar spent.

The damage done by poor experimental design is irreparable. A poor design results in data that contain little information. Consequently, no matter how thorough, how clever, or how sophisticated the subsequent analysis is, little information can be extracted. A good design, for the same expenditure of time, money, and other resources, results in data rich in information. A fruitful analysis is then possible. (Note that analysis is defined as trying to extract all the useful information in the data.)

Two-level factorial and fractional factorial designs can be extremely useful for chemists, chemical engineers, and others who do similar work. One of the best ways for a student to learn about such designs is to set one up, get the data, analyze them, and interpret the results. For a number of years I have had students in our experimental design course undertake such projects.

The main piece of advice I give them is to work on something they care about, something they are really interested in.

Toward the end of an introductory one-semester undergraduate course in statistics, for example, one student said that he was a pilot and that, ever since he started to fly, he had asked instructors and other pilots what he should do if the engine failed on takeoff. He had been told by several people that he should bank the plane, go into a 180° turn, and land on the runway from which he took off. Unfortunately, many different ways of doing this maneuver had been suggested. He successfully organized and executed a replicated 2^3 factorial design with three variables: bank angle, flap angle, and speed. He measured the loss in altitude. He started each test at 1000 feet instead of ground level. The experiment was a success. He learned which combination of factors he should use for his plane, and he discovered the minimum altitude for attempting such a maneuver.

Factorial designs can be understood and run with profit by graduate, undergraduate, senior high school, and junior high school students. Maybe younger students can use them, too. Students can study the baking of cakes, the riding of bicycles, the making of chemicals, the growing of plants, and the swinging of pendulums. Dalia Sredni, when she was a seventh grader, for instance, studied the effects of changing oven temperature, baking time, and the amount of baking soda when making a cake. Students should be told about factorial designs early so that they can study systems that depend on many variables and learn how they work. Using such designs they can discover interesting things, have fun, and be surprised. Our students deserve more of these pleasures. I have included a list of 101 experiments that have been done by students at Wisconsin, to indicate the variety of things that is possible.

I would like to end by congratulating the conference organizers for the excellent job they have done. It is clear that they have worked hard to make things enjoyable and rewarding for those of us who have been fortunate enough to participate.

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Table 1. List of some studies done by students in an experimental design course at the University of Wisconsin—Madison.

variables	responses
1. seat height (26, 30 inches), generator (off, on), tire pressure (40, 55 psi)	time to complete fixed course on bicycle and pulse rate at finish
2. brand of popcorn (ordinary, gourmet), size of batch (1/3, 2/3 cup), popcorn to oil ratio (low, high)	yield of popcorn
3. amount of yeast, amount of sugar, liquid (milk, water), rise temperature, rise time	quality of bread, especially the total rise
4. number of pills, amount of cough syrup, use of vaporizer	how well twins, who had colds, slept during the night
5. speed of film, light (normal, diffused), shutter speed	quality of slides made close up with flash attachment on camera
6. hours of illumination, water temperature, specific gravity of water	growth rate of algae in salt water aquarium
7. temperature, amount of sugar, food prior to drink (water, salted popcorn)	taste of Koolaid
8. direction in which radio is facing, antenna angle, antenna slant	strength of radio singal from particular AM station in Chicago
9. blending speed, amount of water, temperature of water, soaking time before blending	blending time for soy beans

Table 1. continued

variables	responses
10. charge time, digits fixed, number of calculations performed	operation time for pocket calculator
11. clothes dryer (A, B), temperature setting, load	time until dryer stops
12. pan (aluminum, iron), burner on store, cover for pan (no, yes)	time to boil water
13. aspirin buffered? (no, yes), dose, water temperature	hours of relief from migraine headache
14. amount of milk powder added to milk, heating temperature, incubation temperature	taste comparison of homemade yogurt and commercial brand
15. pack on back (no, yes), footwear (tennis shoes, boots), run (7, 14 flights of steps)	time required to run up steps and heartbeat at top
16. width to height ratio of sheet of balsa wood, slant angle, dihedral angle, weight added, thickness of wood	length of flight of model airplane
17. level of coffee in cup, devices (nothing, spoon placed across top of cup facing up), speed of walking	how much coffee spilled while walking
18. type of stitch, yarn guage, needle size	cost of knitting scarf, dollars per square foot
19. type of drink (beer, rum), number of drinks, rate of drinking, hours after last meal	time to get steel ball through a maze
20. size of order, time of day, sex of server	cost of order of french fries, in cents per ounce
21. brand of gasoline, driving speed, temperature	gas mileage for car
22. stamp (first class, air mail), zip code (used, not used), time of day when letter mailed	number of days required for letter to be delivered to another city
23. side of face (left, right), beard history (shaved once in two years—sideburns, shaved over 600 times in two years—just below sideburns)	length of whiskers 3 days after shaving
24. eyes used (both, right), location of observer, distance	number of times (out of 15) that correct gender of passerby was determined by experimenter with poor eyesight wearing no glasses
25. distance to target, guns (A, B), powders (C, D)	number of shot that penetrated a one foot diameter circle on the target
26. oven temperature, length of heating, amount of water	height of cake
27. strength of developer, temperature, degree of agitation	density of photographic film
28. brand of rubber band, size, temperature	length of rubber band before it broke
29. viscosity of oil, type of pick-up shoes, number of teeth in gear	speed of H.O. scale slot racers
30. type of tire, brand of gas, driver (A, B)	time for car to cover one-quarter mile
31. temperature, stirring rate, amount of solvent	time to dissolve table salt
32. amounts of cooking wine, oyster sauce, sesame oil	taste of stewed chicken
33. type of surface, object (slide rule, ruler, silver dollar), pushed? (no, yes)	angle necessary to make object slide
34. ambient temperature, choke setting, number of charges	number of kicks necessary to start motorcycle
35. temperature, location in oven, biscuits covered while baking? (no, yes)	time to bake biscuits
36. temperature of water, amount of grease, amount of water conditioner	quantity of suds produced in kitchen blender
37. person putting daughter to bed (mother, father), bed time, place (home, grandparents)	toys child chose to sleep with
38. amount of light in room, type of music played, volume	correct answers on simple arithmetic test, time required to complete test, words remembered (from list of 15)
39. amounts of added Turkish, Latakia, and Perique tobaccos	bite, smoking characteristics, aroma, and taste of tobacco mixture
40. temperature, humidity, rock salt	time to melt ice
41. number of cards dealt at one time, position of picker relative to the dealer	points in games of sheepshead, a card game
42. marijuana (no, yes), tequilla (no, yes), sauna (no, yes)	pleasure experienced in subsequent sexual intercourse

Table 1. continued

variables	responses
43. amounts of flour, eggs, milk	taste of pancakes, consensus of group of four living together
44. brand of suntan lotion, altitude, skier	time to get sunburned
45. amount of sleep the night before, substantial exercise during the day? (no, yes), eat right before going to bed? (no, yes)	soundness of sleep, average reading from 5 persons
46. brand of tape deck used for playing music, bass level, treble level, synthesizer? (no, yes)	clearness and quality of sound, and absence of noise
47. Type of filter paper, beverage to be filtered, volume of beverage	time to filter
48. type of ski, temperature, type of wax	time to go down ski slope
49. ambient temperature for dough when rising, amount of vegetable oil, number of onions	four quality characteristics of pizza
50. amount of fertilizer, location of seeds (3×3 Latin square)	time for seeds to germinate
51. speed of kitchen blender, batch size of malt, blending time	quality of ground malt for brewing beer
52. soft drink (A, B), container (can, bottle), sugar free? (no, yes)	taste of drink from paper cup
53. child's weight (13, 22 pounds), spring tension (4, 8 cranks), swing orientation (level, tilted)	number of swings and duration of these swings obtained from an automatic infant swing
54. orientation of football, kick (ordinary, soccer style), steps taken before kick, shoe (soft, hard)	distance football was kicked
55. weight of bowling ball, spin, bowling lane (A, B)	bowling pins knocked down
56. distance from basket, type of shot, location on floor	number of shots made (out of 10) with basketball
57. temperature, position of glass when pouring soft drink, amount of sugar added	amount of foam produced when pouring soft drink into glass
58. brand of epoxy glue, ratio of hardener to resin, thickness of application, smoothness of surface, curing time	strength of bond between two strips of aluminum
59. amount of plant hormone, water (direct from tap, stood out for 24 hours), window in which plant was put	root lengths of cuttings from purple passion vine after 21 days
60. amount of detergent (1/4, 1/2 cup), bleach (none, 1 cup), fabric softener (not used, used)	ability to remove oil and grape juice stains
61. skin thickness, water temperature, amount of salt	time to cook chinese meat dumpling
62. appearance (with and without a crutch), location, time	time to get a ride hitchhiking and number of cars that passed before getting a ride
63. frequency of watering plants, use of plant food (no, yes), temperature of water	growth rate of house plants
64. plunger A up (slow, fast), plunger A down (slow, fast), plunger B up (slow, fast) plunger B down (slow, fast)	reproducibility of automatic dilutor, optical density readings made with spectrophotometer
65. temperature of gas chromatograph column, tube type (U, J), voltage	size of unwanted droplet
66. temperature, gas pressure, welding speed	strength of polypropylene weld, manual operation
67. concentration of lysozyme, pH, ionic strength, temperature	rate of chemical reaction
68. anhydrous barium peroxide powder, sulfur, charcoal dust	length of time fuse powder burned and the evenness of burning
69. air velocity, air temperature, rice bed depth	time to dry wild rice
70. concentration of lactose crystal, crystal size, rate of agitation	spreadability of caramel candy
71. positions of coating chamber, distribution plate, and lower chamber	number of particles caught in a fluidized bed collector
72. proportional band, manual reset, regulator pressure	sensitivity of a pneumatic valve control system for a heat exchanger
73. chloride concentration, phase ratio, total amine concentration, amount of preservative added	degree of separation of zinc from copper accomplished by extraction

Table I. continued

variables	responses
74. temperature, nitrate concentration, amount of preservative added	measured nitrate concentration in sewage, comparison of three different methods
75. solar radiation collector size, ratio of storage capacity to collector size, extent of short-term intermittency of radiation, average daily radiation on three successive days	efficiency of solar space-heating system, a computer simulation
76. pH, dissolved oxygen content of water, temperature	extent of corrosion of iron
77. amount of sulfuric acid, time of shaking milk-acid mixture, time of final tempering	measurement of butterfat content of milk
78. mode (batch, time-sharing), job size, system utilization (low, high)	time to complete job on computer
79. flow rate of carrier gas, polarity of stationary liquid phase, temperature	two different measures of efficiency of operation of gas chromatograph
80. pH of assay buffer, incubation time, concentration of binder	measured cortisol level in human blood plasma
81. aluminum, boron, cooling time	extent of rock candy fracture of cast steel
82. magnification, read out system (micrometer, electronic), stage light	measurement of angle with photogrammetric instrument
83. riser height, mold hardness, carbon equivalent	changes in height, width, and length dimensions of cast metal
84. amperage, contact tube height, travel speed, edge preparation	quality of weld made by submerged arc welding process
85. time, amount of magnesium oxide, amount of alloy	recover of material by steam distillation
86. pH, depth, time	final moisture content of alfalfa protein
87. deodorant, concentration of chemical, incubation time	odor produced by material isolated from decaying manure, after treatment
88. temperature variation, concentration of cupric sulfate concentration of sulfuric acid	limiting currents on totaling disk electrode
89. air flow, diameter of bead, heat shield (no, yes)	measured temperature of a heated plate
90. voltage, warm-up procedure, bulb age	sensitivity of microdensitometer
91. pressure, amount of ferric chloride added, amount of lime added	efficiency of vacuum filtration of sludge
92. longitudinal feed rate, transverse feed rate, depth of cut	longitudinal and thrust forces for surface grinding operation
93. time between preparation of sample and refluxing, reflux time, time between end of reflux and start of titrating	chemical oxygen demand of samples with same amount of waste (acetanilide)
94. speed of rotation, thrust load, method of lubrication	torque of taper roller bearings
95. type of activated carbon, amount of carbon, pH	adsorption characteristics of activated carbon used with municipal waste water
96. amounts of nickel, manganese, carbon	impact strength of steel alloy
97. form (broth, gravy), added broth (no, yes), added fat (no, yes), type of meat (lamb, beef)	percentage of panelists correctly identifying which samples were lamb
98. well (A, B), depth of probe, method of analysis (peak height, planimeter)	methane concentration in completed sanitary landfill
99. paste (A, B), preparation of skin (no, yes), site (sternum, forearm)	electrocardiogram reading
100. lime dosage, time of flocculation, mixing speed	removal of turbidity and hardness from water
101. temperature difference between surface and bottom waters, thickness of surface layer, jet distance to thermocline, velocity of jet, temperature difference between jet and bottom waters	mixing time for an initially thermally stratified tank of water