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Title: A QUADRATIC PROGRAMMING ROUTINE FOR THE STATISTICAL ANALYSIS OF GAS CHROMATOGRAPHIC DATA

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Abstract approved: Stephen J. Hawkes

A quadratic programming method was developed for the statistical analysis of gas chromatographic data. The method was applied to three types of flavor extracts, peppermint, hops and brewed tea. The brewed tea data had to be abandoned because of the singularity of its coveriance matrix. In all cases tried the method was able to pick the exact origin of a pure hop or peppermint oil. The method was able to classify blends of hop oils with less than five percent absolute error for hypothetical blended values in proportions from zero to 100 percent of the whole. The results for blends of peppermint oils were not as straightforward. Some blends of peppermint were correctly classified with less than a ten percent absolute error over a greater composition range than others. When one three component blend and one four component blend of the peppermint oil were tried the method

classified them correctly. The method can be applied to any problem in which more than one parameter is needed to produce a classification.

A Quadratic Programming Routine for the Statistical Analysis of Gas Chromatographic Data

by

Stanley Claud Elliott Jr.

A THESIS

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APPROVED:

Redacted for Privacy

Associate Professor of Chemistry

in charge of major

Redacted for Privacy

Assistant Professor of Statistics

Redacted for Privacy

Head of Department of Chemistry

Redacted for Privacy

Dean of Graduate School

Date thesis is presented 10th May 1971

Typed by Barbara Eby for Stanley Claud Elliott Jr.

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A QUADRATIC PROGRAMMING ROUTINE FOR THE STATISTICAL ANALYSIS OF GAS CHROMATOGRAPHIC DATA

INTRODUCTION

The question often asked of analysts is not one related to the determination of a single component of a mixture, but one related to all the components of a mixture. Such questions are origin of an oil, price of an oil, variety of plant which produced the oil, percent composition of similar oils in blends and many others.

What is needed is a good general method that will provide this kind of information for all such problems. The purpose of this study was to investigate such a method.

STATISTICAL CONSIDERATIONS

The problems of interest are ones that can be handled by multivariate statistics. The density function of a multivariate normal distribution of the type of interest may be written in n dimensional space as:

$$(2\pi)^{-\frac{1}{2}n} \left|\sum\right|^{-\frac{1}{2}n} \exp - \tfrac{1}{2}(x-\mu)' \sum^{-1}(x-\mu) \qquad (1)$$

(note that in one dimension this is the familiar Gaussian distribution) where x is the observation vector (i. e. 1xn matrix of observed peak areas for one oil) $\sum$ the covariance matrix of the form:

$$\begin{matrix} \sigma_1^2 & \cdots & \sigma_i\sigma_j \\ \vdots & \ddots & \vdots \\ \sigma_i\sigma_j & \cdots & \sigma_i^2 \end{matrix}$$

and $\sum^{-1}$ its inverse. An inverse is a matrix such that $\sum \sum^{-1} = I$ (2) where I is a identity matrix. A matrix is invertable if and only if it is nxn and nonsingular (the determinant is not zero) μ is the vector of means of the parameters of interest (i. e. relative areas). Now the mean vector could be written as $\alpha_i\mu_i$ where α_i is the proportion of the ith oil and μ_i its mean vector. Then what is needed in our type of problem are estimates of the α's.

The problem can therefore be stated in a mathematical model similar to that of Hartmann and Hawkes (3):

$$\min_{\alpha} (x - \sum \alpha_i \mu_i)' \sum^{-1} (x - \sum \alpha_i \mu_i) \qquad (2)$$

subject to $\sum \alpha_i \leq 1$ and $0 \leq \alpha_i \leq 1$ for all i.

Estimates of μ_i and $\sum^{-1}$ can be determined from data on the pure components. Substituting the estimators back into Equation (1) we obtain:

$$\min (x - \sum \alpha_i \overline{x}_i)' S^{-1} (x - \sum \alpha_i \overline{x}_I \qquad (3)$$

subject to $\sum \alpha_i \leq 1$ and $0 \leq \alpha_i \leq 1$ when the matrix multiplication in Equation (3) is carried out we produce an objective equation, in matrix notation of the form:

$$x'S^{-1}x - 2x'S^{-1}(\sum \alpha_i \overline{x}_i) + (\sum \alpha_i \overline{x}_i) S^{-1} (\sum \alpha_i \overline{x}_i) \qquad (4)$$

or in algebraic notation:

$$A \sum \alpha_i^2 + B \sum \alpha_i \alpha_j + C \sum \alpha_i + D \qquad (5)$$

where A, B, C and D are constants calculated from the $\overline{x}_i$'s, S^{-1} and the observation vector x.

This objective function along with the constraints can be handled by a non-linear programming method to solve for the α's. The O. S. U.

computer center has two possible routines *FLEXI (4) and MSUMT (5, 6, 7). MSUMT being the most desirable in that it uses 1/6 of time that *FLEXI would use to reach a solution, (5 sec vs 30 sec).

METHODOLOGY

In order to evaluate the power of such a method, three different types of flavor extract were chosen because of their availability, though crude oil data should also be amenable to this treatment as should any complex mixture. They were mint oil (Smith et al. (8)), hop oil (Buttery et al. (9)) and extract of brewed tea (Vuataz et al. (10)). In order to simplify our discussion the individual samples were given numbers indicating their origin or variety which will be called oil numbers (i. e. in the mint data all of the U. S. Mid-West oil samples have the number one in common).

The mint oil data was the same as that used by Hartmann and Hawkes (3) from Smith and Levi (8). Smith and Levi's analyses reported fifteen peaks of which we used twelve excluding two because the concentrations were too low and a third being the pure menthol peak to eliminate the effect of dementholation in the original data (Table 1). All peaks in the mint oils were calculated as percents of the totally dementholated oil. The mean vectors (Table 2) for this data were obtained from Hawkes (11), and the inverted covariance matrix (Table 3) calculated by use of a statistical library program (12). The hop (Table 4) and tea data (Table 5) (the tea data first being converted to percent total relative area units) contain too many peaks even after eliminating zero peaks to be used in the program to calculate the $\bar{x}_i$

TABLE 1 MINT DATA

1	1.33	1.66	4.39	13.82	0	3.16	49.78	7.99	5.66	6.99	.83	2.16
2	1.72	1.49	5.61	11.72	0	2.81	50.69	8.75	5.78	7.43	1.32	1.49
3	1.20	1.44	5.74	13.38	0	1.12	50.40	9.41	5.74	8.13	1.28	.80
11	1.42	1.60	7.63	14.72	0	5.68	34.59	7.98	7.27	10.82	4.08	3.02
12	1.22	1.74	6.25	13.39	0	5.73	41.31	6.94	6.25	7.64	3.65	3.99
13	1.13	3.00	6.91	14.07	0	4.88	39.97	6.01	7.88	8.44	1.69	5.82
21	.30	1.77	7.62	14.35	0	15.59	29.58	6.20	6.38	12.22	3.37	1.24
22	1.40	1.93	6.49	13.69	0	14.21	30.01	5.97	5.79	12.99	3.86	1.75
23	1.11	2.36	5.30	22.75	0	10.45	30.16	5.05	4.72	8.93	4.38	2.70
24	1.38	3.15	7.28	12.58	0	18.48	17.50	4.33	7.67	22.81	1.77	2.16
31	1.18	1.52	7.09	13.50	0	10.63	35.43	6.07	5.91	8.94	5.57	2.87
32	1.10	1.57	7.22	12.09	0	13.18	26.37	8.00	6.12	9.57	7.22	4.55
33	1.36	1.70	7.15	13.45	0	11.58	29.97	6.64	6.64	9.53	6.64	3.23
34	1.66	1.83	11.30	14.79	0	10.63	30.07	5.48	5.32	7.98	4.65	3.49
35	1.41	1.56	9.69	15.47	0	8.60	30.63	8.75	5.63	8.75	4.22	3.28
36	1.17	3.02	6.54	12.58	0	10.24	33.22	6.71	5.87	9.23	5.87	4.53
41	1.27	1.31	12.30	15.31	0	3.07	36.71	5.97	7.41	8.32	2.35	3.07
42	1.16	1.35	8.79	16.79	0	3.47	32.61	7.91	8.68	13.31	2.51	2.70
43	.99	1.27	7.95	11.02	0	10.48	28.74	6.87	8.86	17.35	3.43	3.43
44	.87	2.17	9.16	11.83	0	9.66	25.99	9.66	8.83	14.16	3.67	3.33
45	1.31	1.64	6.56	20.32	0	7.38	29.83	7.38	5.90	7.54	4.43	6.72
51	1.26	2.97	6.29	13.48	0	11.14	30.36	5.57	6.83	12.94	4.85	3.41
52	.76	1.82	4.91	9.45	0	14.54	31.08	6.36	7.81	11.99	5.09	5.09
60	1.51	3.76	13.30	1.05	.60	0	45.01	12.80	5.87	7.98	1.66	5.87
61	1.07	2.35	12.46	.43	.64	0	45.89	14.09	5.98	12.17	1.28	5.55
62	.97	1.62	9.70	1.94	1.13	0	44.11	14.06	7.43	11.31	1.29	6.14
63	.66	1.82	9.44	1.16	.66	0	43.36	14.73	7.28	12.25	2.15	7.28
64	1.41	1.41	10.09	1.01	.81	0	46.02	14.13	6.86	12.51	.81	4.64
64	1.76	3.63	12.41	.91	.61	0	44.93	13.46	5.60	8.47	2.27	6.35
65	1.59	4.13	13.66	1.27	.64	0	39.72	11.76	5.08	14.94	1.59	5.72
66	1.43	3.72	13.47	1.43	.57	0	38.68	12.03	5.16	14.33	3.15	6.02
67	1.53	3.67	13.62	.92	.61	0	45.28	13.62	5.81	7.19	1.07	6.58
67	1.36	3.79	12.58	.91	.45	0	44.85	14.24	5.76	8.03	1.52	6.52
71	1.77	3.90	12.05	1.06	.53	0	37.76	10.46	5.85	14.89	2.30	9.22
73	1.17	2.15	10.36	.98	.59	0	41.25	11.53	3.91	13.10	2.15	12.71
75	1.26	2.59	8.21	.91	.61	0	46.99	8.36	3.95	10.34	3.04	12.93
81	1.90	3.48	10.53	1.90	5.86	0	39.57	5.38	7.91	2.06	1.90	10.61
82	1.43	3.02	19.10	1.91	6.05	0	39.00	5.25	7.80	1.91	2.23	11.30
83	1.42	2.36	17.02	2.21	5.67	0	37.67	4.89	7.72	2.36	2.84	15.13
84	1.14	3.41	13.31	1.30	5.52	0	35.74	6.50	7.47	1.95	1.62	18.84
85	1.48	4.44	18.44	1.32	5.93	0	40.99	4.77	7.24	1.48	2.47	10.54
91	1.66	3.64	8.11	.99	3.97	0	42.20	12.58	6.62	1.49	8.11	9.93
92	2.21	3.31	11.36	1.42	4.26	0	46.38	13.72	7.83	1.58	3.79	3.79
93	1.92	2.37	11.49	1.28	4.31	0	45.72	14.04	7.98	1.44	3.67	5.59
94	1.42	2.21	12.77	1.73	3.78	0	42.10	13.09	7.25	3.78	4.89	5.36
0	1.48	3.26	17.77	1.48	1.78	0	29.32	8.29	6.51	18.06	3.26	8.00
0	.23	.69	1.61	.46	.23	0	45.10	4.14	2.99	19.10	1.61	23.93
0	.53	2.37	11.31	.53	2.11	0	45.00	7.10	4.47	18.16	.53	7.10

ZERO AND MENTHOL PEAKS DROPPED AND PEAKS CALCLATED AS PERCENTS OF THE TOTALLY DEMENTHOLATED OIL

OIL NUMBERS ASSIGNED IN ORDER STARTING WITH THE 01-03 GROUP ASSIGNED THE NUMBER 1 GROUP 11-13 ASSIGNED THE NUMBER 2 AND SO ON

Table 2. Mean vectors for mint oils.

1.31	1.57	5.45	13.14	0	2.36	50.29	8.72	5.73	7.52	1.14	1.48
1.26	2.11	6.63	14.23	0	5.43	38.62	6.98	7.13	8.97	3.14	4.28
1.17	2.47	6.82	15.84	0	14.68	26.81	5.39	6.14	14.24	3.34	1.96
1.31	1.37	8.17	13.65	0	10.81	30.95	6.94	5.91	9.00	5.69	3.66
1.09	1.65	8.67	15.17	0	6.81	30.78	7.56	7.94	12.14	3.28	3.85
.81	2.34	5.60	11.46	0	12.84	30.72	5.96	7.32	12.46	4.97	4.25
1.23	2.99	11.72	1.10	.67	0	43.78	13.49	6.08	10.92	1.68	6.07
1.33	2.89	10.21	.98	.58	0	42.00	10.12	4.57	12.78	2.50	11.62
1.47	3.34	17.60	1.73	5.81	0	38.59	5.36	7.63	1.95	2.21	13.28
1.80	2.91	10.93	1.36	4.08	0	44.00	13.36	7.43	2.07	5.11	6.17

ELLIOTT TABLE 3 INVERTED S MATRIC FOR MINT

31.4980195	-0.2734778	3.4094883	3.0087701	-4.7054149	3.5473667	4.2594104	4.1675817	6.1198324	3.7396962	5.3976555	5.9284657
-0.2734778	4.7361271	2.8491466	2.8805958	2.6255618	2.7886828	2.8359551	3.0446312	2.9319207	2.7591360	2.5575960	3.0417566
3.4094883	2.8491466	5.6352223	4.2319336	3.4038498	4.1973786	4.3521256	4.0503020	5.2265262	4.1906676	4.7272743	5.6747973
3.0087701	2.8805958	4.2319336	4.3528205	-1.2656533	4.1947795	3.8269526	3.4645649	4.6575051	3.6613008	3.7156917	4.3600708
-4.7054149	2.6255618	3.4038498	-1.2676533	92.2085714	-1.4957146	.2564766	1.7941364	-3.3813058	1.5010860	2.1471857	4.9209476
3.5473667	2.7886828	4.1973786	4.1947795	-1.4957146	4.6743787	3.8888537	3.4762435	4.2125206	3.5552245	3.5373687	4.3047505
4.2594104	2.8359551	4.3521256	3.8269526	.2564766	3.8888537	4.0280890	3.6739475	4.3235243	3.8313681	3.9695874	4.6740528
4.1675817	3.0446312	4.0503020	3.4645649	1.7941364	3.4762435	3.6739475	4.5956997	3.3688709	3.6279751	3.6536814	4.3551736
6.1198324	2.9319207	5.2265262	4.6575051	-3.3813058	4.2125206	4.3235243	3.3688709	9.0531316	3.7166574	5.4058959	5.5828131
3.7396962	2.7591360	4.1906676	3.6613008	1.5010860	3.5552245	3.8313681	3.6279751	3.7166574	3.9063816	3.7849337	4.5318278
5.3976555	2.5575960	4.7272743	3.7156917	2.1471857	3.5373687	3.9695874	3.6536814	5.4058959	3.7849337	5.5894870	4.9244563
5.9284657	3.0417566	5.6747973	4.3600708	4.9209476	4.3047505	4.6740528	4.3551736	5.5828131	4.5318278	4.9244563	6.4458754

TABLE 4 HOP OIL DATA

EC1	.92	.17	1.00	1.20	58.00	.40	4.40	.55	.23	.41	.08	.35	.46	.20	.40	.81	.01	.12	.04	.08
	.17	.32	.04	0	.28	.60	2.00	1.80	0	1.20	0	.01	.12	.22	.09	3.60	.26	8.80	.15	.20
	.32	.35	1.00	.67	.02	.06	.09	.10	.65	.20	1.50	0	.09	.43	.30	.15				
EC2	.31	.09	.47	.74	41.00	.30	1.90	.39	.16	.42	.04	.23	.53	.13	.18	.67	.03	.20	.04	0
	.15	.34	.19	.21	.25	.64	2.00	1.30	0	.70	.02	.07	.34	.38	.05	8.40	.40	21.00	0	.85
	.90	1.00	1.70	1.60	.21	.25	.28	.90	0	.03	.47	.40	.31	.95	.52	.30				
EC3	.80	.10	.51	1.10	62.00	.71	3.50	.48	.33	.39	.09	.66	.72	.25	.38	1.20	.01	.15	.09	0
	.15	.35	.11	.08	.39	.55	2.50	1.90	0	1.30	0	.03	.12	.39	.10	4.00	.29	9.80	.29	.42
	.49	.38	1.50	.70	.10	.13	.20	.30	0	.04	.11	0	.06	.54	.42	.15				
LC1	.83	.11	.67	.94	59.00	.32	3.70	.39	.27	.38	.03	.50	.52	.19	.23	.61	.02	.09	.02	.02
	.10	.30	.04	.05	.23	.46	1.90	1.90	0	1.10	0	0	.11	.17	.06	4.40	.37	11.00	.30	.45
	.49	.33	1.20	.90	.05	.06	.07	.08	.03	.04	.09	.10	0	.42	.36	.10				
LC2	.41	.07	.79	.86	51.00	.46	2.60	.46	.21	.31	.03	.38	.67	.15	.21	1.10	.01	.15	.05	.05
	.10	.27	.07	.09	.34	.74	4.50	2.10	0	1.40	.02	0	.16	.27	.15	5.10	.45	12.50	.43	.42
	.55	.51	1.60	.95	.13	.20	.14	.22	.20	.22	.38	.25	.23	.74	.57	.25				
LC3	.16	.04	.15	.65	23.00	.57	1.40	.48	.10	.28	0	.15	.75	.38	.15	.97	.01	.25	.06	.05
	.22	.34	.20	.26	.49	1.10	4.50	2.40	0	1.40	0	.07	.31	.42	.12	8.90	.76	24.00	.88	.76
	.86	.98	1.50	1.40	.20	.30	.03	.03	.74	.40	2.00	0	.40	1.40	.83	.50				
BG1	.35	.18	.19	.99	61.00	.18	1.40	.42	.31	.37	.08	.80	.32	.15	.45	.33	.09	0	0	.09
	.08	.17	.03	.04	.04	.14	.68	.68	.58	.25	.03	.16	.70	0	0	6.20	.50	10.30	.57	.64
	.58	.70	.40	.98	.17	.30	.04	0	.88	0	.05	.30	.11	.45	.14	.15				
BG2	.29	.13	.29	1.00	62.00	.18	2.00	.32	.29	.33	.05	.55	.27	.16	.40	.35	.01	0	0	0
	.01	.20	0	0	.06	.08	.70	.85	1.50	0	.01	.07	.20	0	0	6.50	.55	11.00	.37	.64
	.66	1.20	0	.92	.15	.19	0	0	.70	0	.10	.40	.20	.30	0	.18				
BG3	.46	.20	.30	1.20	72.00	.22	2.30	.33	.33	.42	.12	1.10	.33	.20	.60	.45	0	0	0	0
	0	.11	0	0	.02	.02	.59	.68	1.20	0	.08	0	.10	0	0	3.90	.09	6.20	0	.30
	.24	.72	.20	.52	.03	.03	0	0	.26	0	.03	.13	0	.05	.01	.02				
BU1	.47	.21	.47	.89	61.00	.25	1.50	.50	.27	.28	.04	.95	.42	.20	.48	.28	.08	0	.03	.04
	.07	.28	0	0	.08	.12	.77	.59	.12	.14	.93	.02	.14	.03	0	6.70	.20	12.00	0	.60
	.57	.60	.48	.80	.12	.10	0	.28	.40	0	.28	.32	.20	.35	.25	.01				
BU2	.50	.17	.43	1.10	69.00	.26	1.90	.50	.31	.39	.09	1.20	.27	.21	.65	.30	.08	0	.04	.09
	.08	.23	.04	.04	.09	.13	.63	.43	.15	.18	.14	.03	.13	.03	.07	4.50	.20	7.20	0	.44
	.51	.55	.24	.70	.05	.12	.05	.46	.30	0	.28	.18	.12	.31	.11	.11				
FU1	.36	.02	.13	.51	44.00	.14	1.30	.38	.33	0	.01	.30	.31	.25	.34	.26	.03	0	.22	.01
	.20	.19	.25	.24	.01	.68	.72	.76	.20	0	0	.05	.35	0	0	8.20	.30	30.00	.25	.74
	.25	.22	1.00	1.30	.13	.18	0	0	.32	0	.28	.25	.20	.39	.23	.24				
FU2	.34	.05	.12	.68	58.00	.09	.95	.48	.44	0	.02	.20	.20	.15	.53	.18	.03	0	.06	.04
	.12	.12	.02	.04	0	.30	.51	.75	.20	0	0	.03	.15	.02	0	6.20	.20	22.00	.20	.50
	.15	.25	.60	1.10	.08	.10	.02	0	.15	0	.08	.13	.09	.14	.12	.05				
FU3	.47	.10	.70	.67	47.00	.15	1.10	.47	.41	0	.05	.27	.27	.17	.50	.27	.03	0	.01	.04
	.12	.15	.06	.08	.01	.31	.51	.61	.33	0	0	.01	.35	0	0	8.20	.50	26.00	.38	.85
	.29	.48	1.70	1.50	.23	.30	0	0	.40	0	.20	.30	.30	.32	.22	.14				

NUMBERS ARE IN PERCENT RELATIVE AREA
ALL SAMPLES WITH THE SAME TWO LETTERS WERE GIVEN THE SAME OIL NUMBER STARTING WITH
EC1 EC2 EC3 BEING ASSIGNED THE NUMBER 1. NUMBERS 2-5 FOLLOWED IN CONSECUTIVE ORDER.

TABLE 5 TEA DATA AS RECEIVED

L.0,001	1.	4503.	23107.	0.	0.	0.	0.	0.
L.0,002	11741.	46732.	127287.	3054.	0.	48063.	8245.	0.
L.0,003	60138.	651.	7897.	24058.	0.	17077.	0.	5733.
L.0,004	6742.	0.	0.	5629.	0.	0.	0.	60807.
L.0,005	1.	16555.	64824.	9429.	0.	5032.	6326.	0.
L.0,006	23388.	92510.	263305.	7154.	22038.	114979.	32226.	0.
L.0,007	122676.	7358.	23338.	52902.	0.	31702.	0.	11785.
L.0,008	14939.	0.	0.	13501.	0.	0.	0.	139661.
L.0,009	1.	18727.	69774.	0.	0.	5172.	0.	1709.
L.0,010	20896.	88601.	259565.	5591.	0.	112231.	15568.	0.
L.0,011	115408.	1978.	19262.	44081.	0.	28916.	0.	10166.
L.0,012	17011.	0.	0.	10160.	0.	0.	0.	114593.
L.0,013	1.	5728.	25616.	3126.	4148.	3147.	4481.	0.
L.0,014	17492.	63925.	195516.	5813.	12209.	67834.	18469.	3157.
L.0,015	97977.	3489.	13960.	46916.	0.	30886.	0.	12285.
L.0,016	18539.	16490.	0.	13374.	0.	0.	0.	119409.
L.0,017	2.	10992.	43073.	4049.	16970.	0.	5561.	0.
L.0,018	47203.	162743.	332779.	16528.	9315.	64974.	57926.	20945.
L.0,019	456004.	25660.	48255.	57533.	23490.	25557.	0.	12311.
L.0,020	25330.	17003.	0.	11920.	10770.	22187.	0.	163493.
L.0,021	2.	10763.	42819.	0.	13086.	0.	0.	0.
L.0,022	32374.	115638.	284038.	11110.	0.	52419.	43693.	17994.
L.0,023	360022.	18701.	31995.	38866.	0.	22398.	0.	11138.
L.0,024	17306.	4605.	0.	0.	0.	18303.	0.	106093.
L.0,025	2.	24232.	83459.	0.	0.	1400.	4710.	3929.
L.0,026	49902.	171848.	358003.	16842.	19097.	81485.	64539.	24393.
L.0,027	437537.	18617.	40941.	70774.	17087.	35677.	0.	13663.
L.0,028	5369.	1249.	0.	8009.	2286.	20614.	0.	147275.
L.0,029	2.	14593.	58029.	0.	0.	1429.	0.	0.
L.0,030	56587.	201628.	422986.	20916.	23965.	91014.	85757.	34770.
L.0,031	594902.	25409.	48735.	89345.	0.	32375.	0.	20443.
L.0,032	26704.	31349.	27089.	11428.	14033.	30254.	4635.	210709.
L.0,033	3.	0.	0.	0.	0.	272.	0.	0.
L.0,034	30254.	278853.	576470.	0.	0.	122662.	72622.	1344.
L.0,035	1033920.	49598.	62072.	69402.	2178.	62136.	0.	37892.
L.0,036	51032.	48170.	0.	590.	0.	55692.	0.	311200.
L.0,037	3.	0.	22710.	0.	0.	0.	0.	0.
L.0,038	57320.	495306.	983840.	0.	0.	172416.	113752.	12516.
L.0,039	1721464.	74230.	98916.	210892.	70138.	114260.	0.	122552.
L.0,040	147076.	29526.	46228.	56422.	74072.	108474.	29576.	557792.
L.0,041	3.	6004.	114544.	0.	0.	0.	0.	0.
L.0,042	69820.	360856.	663662.	6702.	0.	174424.	73856.	8196.
L.0,043	1010426.	46302.	62120.	92512.	0.	52656.	0.	32244.
L.0,044	49612.	30260.	47968.	8418.	0.	43398.	0.	217676.
L.0,045	3.	0.	51914.	0.	0.	0.	0.	0.
L.0,046	37948.	243728.	475770.	0.	0.	106286.	47980.	3572.
L.0,047	818062.	29032.	40286.	53196.	4436.	43920.	0.	14246.
L.0,048	14092.	0.	0.	17814.	0.	42288.	0.	203566.
L.0,049	4.	0.	21154.	0.	0.	0.	0.	0.
L.0,050	41138.	324260.	760408.	0.	0.	147282.	73566.	8882.
L.0,051	1456450.	60712.	82112.	150950.	24570.	116810.	0.	23214.
L.0,052	26220.	16038.	0.	10668.	0.	55198.	0.	263752.
L.0,053	4.	0.	5360.	0.	0.	0.	0.	0.
L.0,054	14744.	193658.	536642.	0.	0.	84775.	84951.	17283.
L.0,055	1607792.	60510.	102534.	194914.	4977.	84956.	0.	18633.
L.0,056	19458.	23431.	0.	18565.	247.	68727.	0.	321836.
L.0,057	4.	0.	92573.	0.	4418.	0.	0.	0.
L.0,058	95994.	567451.	1168454.	9208.	10678.	248756.	166916.	23894.
L.0,059	2143444.	107192.	154978.	202920.	0.	54882.	0.	0.
L.0,060	24922.	62912.	0.	29586.	0.	96588.	0.	420630.
L.0,061	4.	0.	145690.	0.	8202.	0.	0.	0.
L.0,062	113842.	644704.	1248258.	11806.	0.	294306.	195300.	37572.
L.0,063	2275936.	122180.	190748.	290164.	10770.	86888.	9962.	39098.
L.0,064	50404.	124972.	0.	22400.	0.	110382.	88186.	475816.

M.0,070 DONE
M.0,072 READY.1708/08/17/70.

vector and the S^{-1} matrix. This program (12) will handle a maximum of fifteen variables. So it was necessary to transform the peaks into data values that represent groups of peaks, with the same significance in the decision making process as the original peaks.

This process was accomplished by use of the large factor analysis program (13) of the computer center. This produced ten data values for the tea data (Table 6) and nine data values for the hop data. (It should be noted that in practice the factor matrix needs to be calculated only once for any type of problem.)

It was then discovered that the S matrix for the transformed tea data is singular (the determinant is zero within the limits of the computer) and so the tea data could not be handled by the method described in this paper.

The hop data was satisfactory and the mean vectors and the inverted covariance matrix were calculated with the same program (12) that was used for the tea data (Table 7, hop mean vectors; Table 8, covariance matrix).

In order to verify the power of the method the composition of hypothetical blends were calculated. For example if we want to make a 50-50 blend we pick one oil from one subgroup and one from another then halve each of the data points (i. e. half of area for each peak) for each oil and then add the corresponding data points together to make an observation vector. In the case of the hop data such a vector would be reduced by multiplying by the calculated factor matrix for this data.

TABLE 6 REDUCED TEA DATA

.724770	-2.901931	-4.507309	-0.742580	-1.438081	7.145320	1.160770	-5.451285	-2.841453	-4.235477
1.860656	-6.067580	-25.150159	4.685494	-9.647770	35.504127	-0.360420	-9.382530	-9.801327	-10.781620
.936376	-3.435898	-6.953154	-0.710683	-2.679509	10.977323	1.253766	-7.070983	-3.572815	-5.476995
2.169451	-6.347849	-22.089978	6.204428	-9.225943	30.097012	-0.977375	-6.458045	-11.466847	-10.375544
-0.298111	2.270165	-9.406037	-0.276078	-1.677126	5.131405	-0.036990	-1.965020	3.617703	-0.588240
-0.729572	3.817869	.452826	-3.346172	2.902930	-6.372471	1.012522	-0.593902	7.448194	2.074272
-0.187604	2.120247	-7.246936	-2.015724	-0.465663	5.174237	.827466	-3.633859	4.570957	-1.110969
-0.308625	2.104660	-4.742289	-0.680521	-0.920227	.661515	-0.012083	-1.027811	3.265826	.288649
-0.678245	1.049949	9.399353	-0.777901	4.033642	-11.749833	.012131	4.192809	1.821903	3.821339
-0.178915	-0.787986	3.357576	1.944273	.056755	-7.530247	-0.910095	3.403608	-2.490160	1.621658
-1.307709	2.300667	6.373845	-4.185336	3.573343	-11.324330	1.219349	-0.637600	5.842081	3.904055
-0.955005	1.564187	9.536407	-3.073995	5.033695	-11.569881	.989582	1.724101	4.215699	3.835448
-0.188393	.845583	12.399354	.047788	5.232794	-12.259565	-0.185685	6.308172	.863928	3.510591
.830875	.163616	14.776254	4.371610	4.955489	-11.379862	-1.882137	12.243880	-3.361956	2.944020
-0.830944	2.639004	10.512995	-1.833799	4.181537	-11.597407	.041569	4.262161	4.198613	4.717086
-0.859015	.665297	13.287252	.389198	-3.915865	-10.907342	-2.152370	4.086302	-2.310345	5.851729

Table 7. Mean vectors for hop oils.

33.8432	24.0959	88.5502	49.4387	24.3449
-11.2954	-6.1623	-28.0843	-11.9552	7.3302
-5.2746	-0.6423	35.3283	-11.6449	-0.1461
-0.8254	-1.2747	-36.9993	-1.6220	4.9920
3.1812	2.3600	4.9553	3.0366	3.0336
-3.1759	-1.7595	4.0082	-3.6058	-1.0282
-3.3945	-2.3808	-8.6533	-3.7740	-3.0376
-4.2954	-2.8212	1.4726	-7.0702	-2.6841
-4.0533	-3.3736	-4.5932	-5.9508	-2.9482

TABLE 8 INVERTED COVARIANCE
FOR HOP OILS

ROW 1
3.45369 5.19423 5.23144 5.64690
-9.71961 -20.01592 9.26335 20.38168
-19.42561

ROW 2
5.19423 11.74983 10.23245 4.11720
-17.88107 -41.97387 15.78350 22.61597
-28.85229

ROW 3
5.23144 10.23245 13.57705 8.49748
-16.87906 -47.78705 21.56361 28.61422
-35.23864

ROW 4
5.64690 4.11720 8.49748 16.16514
-12.72788 -26.31707 14.92093 45.37401
-36.55000

ROW 5
-9.71961 -17.88107 -16.87906 -12.72788
31.84700 65.00141 -26.38276 -50.29630
55.76190

ROW 6
-20.01592 -41.97387 -47.78705 -26.31708
65.00141 191.81190 -75.48127 -117.76941
129.90248

ROW 7
9.26335 15.78350 21.56361 14.92093
-26.38276 -75.48127 49.33841 55.35416
-66.14813

ROW 8
20.38168 22.61597 28.61422 45.37401
-50.29630 -117.76939 55.35416 164.56656
-130.93840

ROW 9
-19.42561 -28.85229 -35.23864 -36.55000
55.76190 129.90248 -66.14813 -130.93840
131.57625

ROW 1
3.45369 5.19423 5.23144 5.64690
-9.71961 -20.01592 9.26335 20.38168
-19.42561

ROW 2
5.19423 11.74983 10.23245 4.11720
-17.88107 -41.97387 15.78350 22.61597
-28.85229

ROW 3
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-35.23864

ROW 4
5.64690 4.11720 8.49748 16.16514
-12.72788 -26.31707 14.92093 45.37401
-36.55000

ROW 5
-9.71961 -17.88107 -16.87906 -12.72788
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55.76190

ROW 6
-20.01592 -41.97387 -47.78705 -26.31708
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129.90248

ROW 7
9.26335 15.78350 21.56361 14.92093
-26.38276 -75.48127 49.33841 55.35416
-66.14813

ROW 8
20.38168 22.61597 28.61422 45.37401
-50.29630 -117.76939 55.35416 164.56656
-130.93840

ROW 9
-19.42561 -28.85229 -35.23864 -36.55000
55.76190 129.90248 -66.14813 -130.93840
131.57625

Data of pure oils and of blends were then used to calculate objective equations and subject to the minimization routine.

RESULTS AND DISCUSSION

The results for the hop oils (Table 9) were done by two routines *FLEXI and MSUMT. The method was able to exactly pick which group the pure oil belonged to. The MSUMT routine was able to classify the mixture within five percent of the hypothetical blended value for the nine blends tried ranging in values from ten to 90 percent of the whole.

The mint data can be divided into two groups, those numbered one through six (Mentha piperita oils) which contain no octanol but do contain menthofuran and those numbered seven through ten (Mentha arvensis oils) which contain octanol but no menthofuran. The routine MSUMT was used for all mint classifications.

Mentha Arvensis Oils (Seven-Ten)

An oil from group seven (Brazilian) and one from group nine (Japanese) were chosen at random and the routine classified them unambiguously, estimating the fraction of the oil coming from other origins at less than 0.01 percent in the Brazilian and less than two percent in the Japanese.

The routine was then used to find the concentration of these oils in hypothetical blends with each other and with oils from other origins,

Table 9. Hop oils.

Oil Numbers				
1	2	3	4	5
		*FLEXI		
1.00				
1.0000				
.50			.50	
.4338			.5021	.0639
.90			.10	
.8790		.0021	.0985	.0019
		MSUMT		
.10			.90	
.0895		.0049	.9047	
.20			.80	
.1871		.0028	.8093	
.30			.70	
.2849			.7134	
.40			.60	
.3825			.6169	
.50			.50	
.4601	.0002	.0031	.5181	
.40			.40	
.5610	.0002	.0016	.4218	
.70			.30	
.6617	.0002	.0008	.3247	
.80			.20	
.7703		.0001	.2271	
.90			.10	
.8684			.1295	

with up to three other oils in any one blend. Of the 27 hypothetical two component blends and one three component blend of these oils with other oils ranging in value from 30 to 95 percent of the whole for oil number seven and 45 to 95 percent of the whole for oil number nine, the absolute error was less than two percent. In the case of the four component blend (which contained two piperita oils which are discussed in the next section) the absolute error was less than two percent for oil nine and less than four percent for oil seven (Table 10).

Mentha Piperita Oils (One-Six)

The classifications between oils from origins one through six were not as good. The results seem to depend on which pair is used to make up the mixture. For instance in the classification between origins one (U. S. Mid-West) and origin seven (Brazilian) the absolute errors range from five percent when the hypothetical percentage for component one was five percent of the whole to less than three percent when the hypothetical value was 70 percent.

In the case of ten blends of origin one and four (Italian) the routine was able to classify this pair with absolute errors of less than seven percent when the hypothetical percentage of oil four was 40 percent of the whole to less than three percent when the hypothetical percentage was 95 percent. The absolute error for origin one varied from 12 percent when the hypothetical percentage of the oil was 20 percent

Table 10. Blends of mentha piperita with mentha arvensis oils.

Oil Numbers									
1	2	3	4	5	6	7	8	9	10
0						1.00			
						1.000			
.05						.95			
.0004			.0291			.9705			
.10						.90			
.0587			.0222			.9190			
.15						.85			
.1124			.0183			.8692			
.20						.80			
.1650	.0036		.0120			.8193			
.25						.75			
.2173	.0080		.0053			.7694			
.30						.70			
.2695	.0109					.7196			
.35						.65			
.3228	.0071					.6700			
.40						.60			
.3761	0034					.6205			

Table 10 continued.

Oil Numbers									
1	2	3	4	5	6	7	8	9	10
.45						.55			
.4290						.5760			
.50						.50			
.4787						.5213			
.55						.45			
.5282						.4717			
.60						.40			
.5778						.4217			
.65						.35			
.6274						.3726			
.70						.30			
.6770						.3230			
			0					1.00	
			0				.0132	.9868	
			.05					.95	
			0	.0502			.0120	.9376	
			.10					.90	
			0	.1040			.0069	.8891	

Table 10 continued.

				Oil Numbers					
1	2	3	4	5	6	7	8	9	10
			.15					.85	
			0	.1576			.0018	.8406	
			.20					.80	
			.0343	.1743				.7914	
			.25					.75	
			.0981	.1601				.7418	
			.30					.70	
			.1618	.1601				.6922	
			.45					.55	
			.3535	.1030				.5432	
			.50					.50	
			.4174	.0887				.4939	
			.55					.45	
			.4813					.4443	
		0						1.00	
								.9868	
		.05						.95	
			0509				.0120	.9371	

Table 10 continued.

Oil Numbers									
1	2	3	4	5	6	7	8	9	10
		.10						.90	
			.1053				.0063	.8882	
		.15						.85	
			.1594				.0012	.8393	
		.20						.80	
			.1800					.7894	
		.25						.75	
			.0899	.1705				.7396	
		.30						.70	
		.1425	.0156	.1543				.6893	
.05		.15				.80			
.1098	.0088	.0657				.8157			
		.25		25		.25		.25	
.1010		.1242	.0493	.2467		.2160		.2627	

to less than three percent when the hypothetical percentage was 60 percent (Table 11). Fouteen other hypothetical blends tried are shown in (Table 12). Thirteen of these blends were from origin three (Yakima Valley) and five (English). In these blends the sum of the values picked by the routine from origin one and three is quite close to the hypothetical value for origin three (.3100 when the hypothetical value was 30 percent). This can be expected since the plants that produced both of these oils were descended from Italian plants and the weather in both areas is similar. However it should be noted that if all U. S. origins were lumped together, the method would be able to exactly classify such a category. The same problem arises in the cases of the three component blend and the four component blend. Note in the case of the four component, the absolute error for origin five is less than one percent, while that for origin three is not as good. (Note lumping origin one and three together would produce an absolute error of less than three percent for such a origin.) This method is the first to the author's knowledge to classify three and four component blends.

When blends of oils one and four with five percent of oil seven blended in were tried, it was found that an absolute error in the value for the number four oil in the 55 to 95 percent range was reduced to within five percent (Table 13). This could mean that the value of some oils could be improved by spiking in certain other oils. If this was

Table 11. Blends of mentha piperita origins one and four.

Oil Numbers									
1	2	3	4	5	6	7	8	9	10
)			1.00						
			.9295		.0694				
.05			.95						
			.9257		.0727				
.20			.80						
.0825	1323		.7682		.0159				
.30			.70						
.2024			.6757						
.35			.65						
.2630	.1137		.6232						
.40			.60						
.3215	.1112		.5673						
.45			.55						
.3793	1103		.5105						
.50			.50						
.4405	.0972		.4523	.0100					

Table 11 continued.

Oil Numbers									
1	2	3	4	5	6	7	8	9	10
.55			.45						
.5098	.0551		.3911	.0439					
.60			.40						
.5791	.0132		.3300	.0776					

Table 12. Other blends of mentha piperita.

Oil Numbers									
1	2	3	4	5	6	7	8	9	10
		0		1.00					
.0590				.9392					
		.05		.95					
.0697				.9278					
		.10		.90					
.0804				.9163					
		.15		.85					
.0912				.9048					
		.20		.80					
.0999		.0320		.8650					
		.25		.75					
.1100		.1335		.7518					
		.30		.70					
.1158		.1842		.6953					
		.35		.65					
.1250		.2350		.6388					
		.40		.60					
.1176		.2866		.5612					

Table 12 continued.

Oil Numbers									
1	2	3	4	5	6	7	8	9	10
		.45		.55					
.1154		.3342	0183	.4781					
		.50		.50					
.1184	.0508	.3684	.0652	.3926					
		.55		.45					
.1264	.0500	.4045	.1122	.3075					
		.60		.40					
.1215	.0585	.4417	.1572	.2168					
.50				.50					
.4405	.0971			.4523	.0101				

Table 13. Blends of origin one and four with five percent seven.

Oil Numbers									
1	2	3	4	5	6	7	8	9	10
0			.95			.05			
0	.0342		.9620						.0038
.05			.90			.05			
	.1145		.8807						.0041
.10			.85			.05			
.0080	.1831		.8032						.0046
.15			.80			.05			
.0694	.1722		.7519						.0057
.20			.75			.05			
.1257	.1613		.7026			.0051			.0041
.25			.70			.05			
.1814	.1501		.6537			.0107			.0039
.30			.65			.05			
.2351	.1416		.6034			.0174			.0025
.35			.60			.05			
.2876	.1351		.5521			.0244			.0008
.40			.55			.05			
.3413	.1296		.4994			.0298			

Table 13 continued.

					Oil Numbers				
1	2	3	4	5	6	7	8	9	10
.45			.50			.05			
.3916	.1412		.4476			.0335			
.50			.45			.05			
.4576	.0981		.3898	.0174		.0370			

proven to be true the routine could be used to determine which oils and their percentage to spike in.

It should be noted that an error in classification does not mean necessarily a wrong answer but the possibility of producing the sample by the blend picked. It should be noted that all of the oils numbered one through six are botanically related being descended from English plants so that some difficulty in their classification can be expected.

CONCLUSION

The quadratic minimization routine seems to be a promising method to handle gas chromatographic data to answer such questions as compositions of blends of oils. The whole data handling package can be combined to produce rapid answers by interfacing a gas chromatograph with a computer. Greater accuracy could be obtained by obtaining data with the accuracy needed for the desired problem.

The method could be applied to any problem that produces several measurable parameters subject to natural variations.

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APPENDIX

APPENDIX

Explanation of Sample Input File-Appendix Table 1

The sample input file shown is for a mint blend. The file can be divided into two parts. The first half which would not change for any mint blend problem contains control parameter cards for MSUMT. The inequality constraints are contained in this part of the file. The second half of the file contains the A vector, the B matrix of Equation (5) of the main text and a vector of zeros. The vector of zeros contains one zero for each α_i. The format for this half of the input file is 8F10.5. Several files of different problems like hop and mint oils or several groups of origin problems can be combined, the advantage being that only one loading operation need be carried out instead of several.

The input files are set up as the example to take advantage of a compiled program called *USERSUB that will generate the objective functions and their gradients. *USERSUB eliminates the need to write input programs for MSUMT.

If one has only one type of problem (i. e. only origin of mint oil) a program could be written that would only require that raw data be entered to produce an output.

Following the table is a sample output. For further information see the MSUMT write up available at O. S. U. Computer Center.

```
  APPENDIX TABLE 1 SAMPLE INPUT FILE FOR MSUMT ROUTINE
 1=0 4=.95 7=.05
   10    0    0   21   20    0    0    0         0.
   1.E-06    1.E-08    1.E-05
     0.04    0.0001      0.15    0.0001    0.0001      0.80    0.0001    0.0001
   0.0001    0.0001
   1  -1   2  -2   3  -3   4  -4   5  -5   6  -6   7  -7   8  -8   9  -9  10 -10
       0.       -1.        0.       -1.        0.       -1.        0.       -1.
       0.       -1.        0.       -1.        0.       -1.        0.       -1.
       0.       -1.        0.       -1.
      -1.       -1.       -1.       -1.       -1.       -1.       -1.       -1.
      -1.       -1.
      -1.
-776.15361-783.84127-777.05241-777.34254-786.85320-781.36755-787.13007-792.45889
-770.34967-765.53631
 388.65814 391.75873 387.95145 388.06438 392.97513 390.11278 394.31980 396.94688
 384.20601 382.56931 391.75873 395.43802 391.68891 391.85876 396.86721 393.94444
 397.48854 400.21290 388.80049 386.33563 387.95145 391.68891 389.11895 388.55481
 393.24581 390.75209 392.20948 394.76543 382.23936 380.23169 388.06438 391.85876
 388.55481 388.62263 393.37093 390.63960 393.52376 396.19353 385.07285 382.61243
 392.97513 396.86721 393.24581 393.37093 398.44937 395.46133 398.71562 401.42015
 390.36981 387.62767 390.11278 393.94444 390.75209 390.63960 395.46133 392.81044
 395.29719 397.96042 386.50080 384.04660 394.31963 397.48835 392.20926 393.52358
 398.71542 395.29703 404.39774 407.45446 401.80281 397.07786 396.94672 400.21274
 394.76525 396.19337 401.41997 397.96029 407.45446 410.85875 406.06243 400.54068
 384.20448 388.79883 382.23752 385.07126 390.36805 386.49947 401.80271 406.06233
 429.06952 411.84300 382.56824 386.33447 380.23040 382.61132 387.62643 384.04567
 397.07778 400.54062 411.84301 400.72465
         0         0         0         0         0         0         0         0
         0         0
```

```
T H I S   I S   A   SUMT-PWL   R U N   F O R   1=0 4=.95 7=.05

INEQUALITY CONSTRAINTS      0 EQUALITY CONSTRAINTS      0

LINEAR CONSTRAINTS    21, BOUNDS    20, EQUALITIES     0
          SCALE FACTOR IS   1.00000000E 00

THE STARTING VECTOR IS

 4.00000000E-02  1.00000000E-04  1.50000000E-01  1.00000000E-04  1.00000000E-04  8.00000000E-01  1.00000000E-04
 1.00000000E-04  1.00000000E-04  1.00000000E-04

LINEAR CONSTRAINTS VALUES
   4.00000000E-02  9.60000000E-01  1.00000000E-04  9.99900000E-01  1.50000000E-01  8.50000000E-01  1.00000000E-04
   9.99900000E-01  1.00000000E-04  9.99900000E-01  8.00000000E-01  2.00000000E-01  1.00000000E-04  9.99900000E-01
   1.00000000E-04  9.99900000E-01  1.00000000E-04  9.99900000E-01  1.00000000E-04  9.99900000E-01  2.94091823E-03

FUNCTION COUNT =      0 SUMT-POWELL VALUE = -3.88522804E 02 UNSCALED FUNCTION VALUE = -3.88522804E 02 SUMT RK =  1.00000000E 00

                          * * * * * * * * * * * * * * * * * * * * * * *
                          *                                           *
                          *           FINAL SOLUTION REPORTS          *
                          *                                           *
                          * * * * * * * * * * * * * * * * * * * * * * *

FUNCTION COUNT =    25       THE MINIMIZED OBJECTIVE VALUE =  -3.88720761E 02       SUMT RK =   1.00000000E 00

THE FINAL X VALUES
  -8.64899170E-11  3.41775361E-02  2.05221196E-10  9.61950004E-01 -2.16211932E-11 -2.31575557E-10 -3.80232679E-10
  -2.92235062E-10  2.97609137E-10  3.77096082E-03

INEQUALITY CONSTRAINTS      0 EQUALITY CONSTRAINTS      0  AT THE STAGE OF TERMINATION

LINEAR CONSTRAINTS    21, BOUNDS    20, EQUALITIES     2

LINEAR CONSTRAINT VALUES(INCLUDE BOUNDS)
  -8.64899170E-11  1.00000000E 00  3.41775361E-02  9.65822464E-01  2.05221196E-10  1.00000000E-00  9.61950004E-01
   3.80409057E-02 -2.16211932E-11  1.00000000E 00 -2.31575557E-10  1.00000000E 00 -3.80232679E-10  1.00000000E 00
  -2.92235362E-10  1.00000000E 00  2.97609137E-10  1.00000000E-00  3.77096082E-03  9.96229039E-01  1.01499259E-04

CUMULATIVE EXECUTION TIME =    5.100 SECONDS

                              THESE ARE FINAL ANSWERS
```

SYMBOLS

α_i	The proportion of the ith pure component
μ_i	Vector of means of parameters of interest
Σ	The variance-covariance matrix
Σ^{-1}	The inverse of the variance-covariance matrix
$\sum$	Summation symbol
x	The observation vector
$\bar{x}_i$	Estimator of μ_i
S^{-1}	Estimator of Σ^{-1}