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Pattern Recognition Analysis of Elemental Data. Wines of *Vitis vinifera* cv. Pinot Noir from France and the United States

Wing-On Kwan, Bruce R. Kowalski,* and Rodney K. Skogerboe

Forty wines of *Vitis vinifera* cv. Pinot Noir from France, California, and the Pacific Northwest region of the United States were analyzed for 17 elements by atomic emission spectrometry. Intercorrelations among these elements and their relations to geographic origins were investigated by analyzing the elemental data with pattern recognition techniques. A distinct difference was found between the levels of aluminum in California and Pacific Northwest samples, while barium was the key element in distinguishing French Pinot Noirs from those produced in the United States. Differences in elemental concentrations due to intraregional and vintage variations were also identified.

Wine contains a wide variety of inorganic constituents and many of them are significant in the wine-making process. Lists of major inorganic components in wine have been compiled by Amerine and Joslyn (Amerine, 1958; Amerine and Joslyn, 1970). Although some trace elements have been found to be important to stability and quality (Amerine et al., 1967), the roles of many minor and trace elements are still obscure and little is known about their interrelationships. In order to gain an overall view of the mineral content of wine, more quantitative information on trace elemental profiles of wines must be obtained.

Elemental concentrations in wines are affected by many factors. One major source of supply of elements is soil from which the grapes get their nourishment. Diversities of soil types in various wine regions can, therefore, be reflected in the differences in elemental concentrations of wines produced. Two other major factors are grape variety and climate condition which is subject to both regional and seasonal variations. Other variables such as time of harvest, temperature of fermentation and storage, time of storage, use of fining agents, filter aids, ion-exchange resins, and even bottling practices all contribute to the elemental concentration in the resulting wine. But these factors, which collectively can be very significant, tend to offset the effect of each other, thus making it difficult to characterize wines according to geographic origins by their elemental concentrations.

The use of an atomic emission spectrometer coupled with a data acquisition system enables enologists to obtain reliable multielemental data of wine rapidly and efficiently. Because of the fast rate at which elemental data can be generated, reducing the massive amount of data to meaningful information has become a major task for enologists. Different mathematical methods of data analysis have been

applied to enological studies (Wu et al., 1977) and other areas of food science (Powers and Keith, 1968; Young et al., 1970). One aid to data reduction and trend detection is pattern recognition (Jurs and Isenhour, 1975; Harper et al., 1977), which is a collection of computer-based data manipulation techniques. Its first successful application in enology was done by Kwan and Kowalski (1978), and an example of using these techniques to recognize patterns in trace elements has been published by McGill and Kowalski (1977). Pattern recognition has also been proven successful in a wide variety of chemical problems. General reviews of its theory and application in chemistry have been published by Kowalski (1975) and Jurs and Isenhour (1975). In general, pattern recognition can be applied to problems where there is a collection of objects and a list of measurements made on each object. The question to be answered will then be whether it is possible to find and/or predict a property of the objects that is not directly measurable but is known to be related to the measurements via some unknown relationship.

The purpose of this study was to provide quantitative information for several major and trace elements of selected wines of *Vitis vinifera* cv. Pinot Noir from three wine regions, namely, France, California, and the Pacific Northwest region of the United States. Atomic emission spectrometry was used for the simultaneous determination of 17 elements. Pattern recognition techniques were employed to extract key elements and combinations of elements which were characteristic of geographic origins and to investigate subtle differences in elemental concentrations due to intraregional and vintage variations.

EXPERIMENTAL SECTION

Forty wine samples of *Vitis vinifera* cv. Pinot Noir were selected for analysis. There were 9, 17, and 14 samples from different wineries in the state of California, Pacific Northwest region of the United States, and France, respectively. The Pacific Northwest region consists of the states of Washington and Oregon which have similar climate and soil types. A detailed description of these samples is given in Table I. The wines were analyzed by

Laboratory for Chemometrics, Chemistry Department, University of Washington, Seattle, Washington 98195 (W.K., B.R.K.), and the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521 (R.K.S.).

Table I. Description of 40 Selected Wine Samples

France	
Drouhin, Beaune-Greves	1972 ^a
Drouhin, Volnay-Clos des Chenes	1972
Gevrey-Chambertin, Clos du Chaptire Brocard	1972
Givry, Domain Baron Therard	1969
	1970
	1971
	1972
Grand Eschezeaux (Domain Romanee Conti)	1962
(unknown estate)	1971
Jaffelin Bourgogne du Chaptire	1972
Ponnelle, Chambolle-Musigny	1972
Ponnelle, Chassagne-Montrachet	1972
United States	
California	
David Bruce (lot 1)	1973 ^b
Freemark Abbey	1970
Lords & Elwood	1973
Louis Martini	1973
Robert Mondavi	1973 ^b
Simi	1973
Stonegate	1975
Pacific Northwest	
Washington	
Associated Vintners	1966
	1967
	1968
	1969
	1970 ^c
	1971
	1972
	1973
	1974
	1968
Ste Michelle	
Oregon	
Erath	1975
Eyrie	1974
Ponzi	1975
Salishan	1974

^a Three different bottles. ^b Two different bottles.

^c Four different bottles.

atomic emission spectrometry and the instrument used was a commercial D.C. three-electrode plasma echelle spectrometer system (Spectrascan III, Spectrametrics, Inc.) at the Department of Chemistry, Colorado State University. The spectrometer system was designed for simultaneous determination of 17 elements, namely, aluminum, barium, boron, cadmium, calcium, chromium, copper, lead, magnesium, manganese, molybdenum, nickel, phosphorus, potassium, silicon, sodium, and strontium. ACS reagent grade chemicals were used as elemental standards for each element. Sample dilutions were prepared with deionized distilled water containing 12% ethanol. Four replicate measurements were obtained for each element from each wine sample. The average of the replicates and the standard deviation were recorded for each and used in computer analysis.

The data were analyzed using our research version of ARTHUR (Harper et al., 1977) which contains more than 40 statistical and pattern recognition methods written in Fortran. A version of this system is available upon request (Duewer et al., 1976). All processing was done on the University of Washington Academic Computer Center's CDC 6400 computer.

Terminologies in pattern recognition used throughout this study are defined as follows. Each individual wine sample analyzed is an "object" and each of the 17 elemental compositions is a "measurement". The measurements are used to generate "features" which may be the simple measurements as in this study, or they may be some combinations of measurements, mathematical transformations

of the measurements, and/or combinations of the above. The feature values define a "data vector" for each of the objects. When data vectors belong to defined groups, such as geographic origins in this study, the groups are called "categories".

The pattern recognition techniques used in the study are largely nonparametric, making no or minimal assumptions about the underlying statistics of the data, and are insensitive to the nature of the data as long as it is numerical. Methods used are listed as follows: AUTOSCALE (Kowalski and Bender, 1972), correlation matrix, WEIGHT (Kowalski and Bender, 1972), SELECT (Kowalski and Bender, 1976), KARHUNEN-LOEVE (K-L) TRANSFORM (Kowalski and Bender, 1972), least-squares multilinear regression analysis (LEAST) (Harper et al., 1977), K-nearest neighbor analysis (KNN) (Cover and Hart, 1967), and statistical iso-linear multiple component analysis (SIMCA) (Wold, 1976).

RESULTS AND DISCUSSION

Simple statistics on the measurements of elemental concentrations of wine samples from France, the United States, California, and the Pacific Northwest are shown in Table II. Examination of these data, however, does not reveal any obvious characteristics reflecting geographical origins of the samples. However, it is quite interesting to note that even among the great diversity of wines used in this study, the ranges and magnitudes of the elemental concentrations are comparable. Trace elements, aluminum, barium, cadmium, chromium, copper, molybdenum, nickel, lead, and strontium are all present at levels below 1 mg/mL, while boron and manganese have concentrations between 1 and 100 mg/mL. The next higher level which is between 10 and 100 mg/mL is occupied by calcium, sodium, and silicon. Phosphorus and magnesium contents are generally above 100 mg/mL and potassium, which constitutes about three-fourths of the total cation content in wines, has a concentration of about 1000 mg/mL.

Interdependence of these elements are shown in Table III in the form of a correlation matrix. Positive correlations over the entire data set above 0.5 are observed for the following measurement combinations (Ba, Mg, Sr), (Ba, K, Sr), (K, Na, Sr), (Ca, Si), (Si, K), and (Mo, Pb). The magnitudes of these correlations are not so high, except for (Pb, Mo), that one measurement can be used in place of another, nor can they be considered as independent. Generally, in many types of sedimentary rocks and minerals deposited in them, calcium, potassium, magnesium, and silicon are present as major constituents while barium and strontium are trace constituents usually associated with them. The correlations of these elemental concentrations in wine reflect their close associations in soil and availability for simultaneous uptake by the grape plant.

Six classifications of various combinations of the three wine regions were attempted and the importance of each element in distinguishing one region from another was determined by the magnitudes of their variance weights. Generally, cadmium, copper, manganese, molybdenum, lead, and sodium had low variance weights thus contributing insignificantly to the regional classifications. High variance weight features included barium, potassium, magnesium, silicon, and strontium. The process SELECT picked out the three most important, but independent, features for each of the six classifications which are shown in Table IV. The variance weights of the first selected features are much higher than those of the second and third selected features. This suggests that the first selected features contain most of the information necessary for the respective classifications. Based on these results, aluminum is chosen as the key feature in separating samples

Table II. Concentrations of 17 Elements for Wines from the United States, France, the Pacific Northwest Region, and California

	United States ^a			France		
	range ^b	av ^b	SD ^b	range ^b	av ^b	SD ^b
Cd	0.005-0.106	0.050	0.020	0.009-0.087	0.049	0.022
Mo	0.030-0.479	0.167	0.098	0.009-0.415	0.181	0.119
Mn	0.906-4.080	1.811	0.505	1.150-2.320	1.646	0.315
Ni	0.051-0.466	0.078	0.035	0.041-0.077	0.058	0.013
Cu	0.050-0.830	0.149	0.114	0.043-0.552	0.179	0.133
Al	0.380-1.350	0.776	0.449	0.512-2.070	0.950	0.489
Ba	0.158-0.408	0.176	0.098	0.071-0.225	0.108	0.042
Cr	0.006-0.100	0.049	0.022	0.021-0.063	0.042	0.016
Sr	0.720-2.910	0.738	0.683	0.156-1.130	0.361	0.273
Pb	0.171-2.060	0.777	0.470	0.025-1.850	0.830	0.569
B	2.000-8.110	5.800	1.363	3.790-7.500	5.700	1.191
Mg	99.300-208.000	119.830	34.225	75.900-148.000	102.271	18.755
Si	4.570-43.600	14.049	10.272	6.000-13.000	8.374	2.121
Na	7.250-125.000	36.043	29.701	10.400-59.700	28.307	19.405
Ca	58.300-128.000	68.678	13.521	44.900-83.800	62.207	10.422
P	81.900-266.000	167.478	33.563	132.000-211.000	153.929	22.369
K	924.000-1810.000	1126.957	241.725	820.000-1240.000	984.286	115.339

	Pacific Northwest			California		
	range ^b	av ^b	SD ^b	range ^b	av ^b	SD ^b
Cd	0.005-0.106	0.052	0.032	0.013-0.068	0.051	0.018
Mo	0.044-0.479	0.203	0.118	0.030-0.211	0.146	0.052
Mn	0.906-4.080	1.517	0.767	1.470-3.140	2.067	0.646
Ni	0.051-0.466	0.137	0.114	0.058-0.166	0.109	0.035
Cu	0.051-0.830	0.187	0.268	0.050-0.210	0.103	0.057
Al	0.465-1.350	1.024	0.286	0.308-0.889	0.505	0.174
Ba	0.158-0.408	0.291	0.078	0.181-0.349	0.281	0.054
Cr	0.006-0.072	0.038	0.016	0.028-0.100	0.060	0.025
Sr	0.794-1.350	1.062	0.150	0.720-2.910	1.323	0.727
Pb	0.206-2.060	1.025	0.522	0.171-1.020	0.696	0.260
B	2.000-6.560	3.664	1.254	3.500-8.110	5.954	1.660
Mg	112.000-193.000	143.176	21.340	99.300-0.208	147.144	35.648
Si	4.570-19.700	14.196	5.155	9.180-43.600	22.878	11.782
Na	7.250-101.000	47.851	30.146	12.500-125.000	48.078	39.323
Ca	58.300-128.000	85.506	20.753	59.500-95.200	78.744	11.788
P	81.900-187.000	136.559	43.833	141.000-266.000	188.556	38.256
K	924.000-1290.000	1094.529	96.862	1030-1810.000	1348.889	219.171

^a Combination of Pacific Northwest and California. ^b Concentration in microgram/milliliter.

from the Pacific Northwest and California while barium is important in classifications involving separations of samples from France with those from either one or both wine regions in the United States.

Three classification methods, LEAST, KNN, and SIMCA, were also used to classify samples according to their geographic origins. When all 17 features were used, perfect classification was achieved. But the low sample/measurement ratio raised some doubts on these results. Ideally, the ratio should be at least 4 or preferably much higher, and this was attained when only a few selected features were used as elemental profiles for the samples. Comparisons of three classification methods in Table IV showed that all three worked quite well for this problem but LEAST achieved slightly better results than the others. The classification results obtained from LEAST using only the first selected feature are high and this agrees with the earlier observation that one element contains sufficient information to separate wines from different regions. The only exception is the simultaneous separation of samples from France, California, and the Pacific Northwest.

Results from SELECT and the three classification methods clearly reinforce the findings of each other. It is then concluded that barium is the key element in the 17-element profile used to distinguish French Pinot Noir from American Pinot Noir and aluminum is the best element for characterization of the elemental difference between Pinot Noir from California and the Pacific Northwest. A close examination of the levels of these two key elements

in Table II shows that French Pinot Noir has on the average a lower level of barium than American Pinot Noir. On the other hand, Pinot Noir from California has an aluminum concentration twice as high as their counterparts from the Pacific Northwest which may be due to the nature of the clay soils in California.

In this study, the measurement uncertainties were known so there existed a matrix of uncertainties corresponding to, and of the same dimensions as, the data matrix. Therefore, each measurement in the data matrix was treated as a mean value with a probability distribution defined by its error. The pattern recognition programs used in this study allowed the inclusion of these uncertainties into the analysis (Harper et al., 1977). Classification results of French and American samples, with and without experimental errors included were compared. As shown in Table IV, the inclusion of experimental errors in the data analysis, in this case, had little effect on the classification results. This could best be explained by the fact that the measurements in this study were taken with such excellent precision that the experimental errors become relatively insignificant.

Since the key elements in this data set have been found, they can also be examined by two-dimensional plots. K-L projection of the entire data set from 17 dimensional space onto two dimensions preserving 40% of the total variance is shown in Figure 1. Simultaneous classification of wines from France, the Pacific Northwest, and California using Figure 1 is not successful due to close similarities between

Table III. Correlation Matrix of 17 Elemental Concentrations for 40 Wine Samples

	Al	B	Ba	Ca	Cd	Cr	Cu	K	Mg	Mn	Mo	Na	Ni	P	Pb	Si	Sr
Al	1.000																
B	-0.246	1.000															
Ba	0.020	-0.332	1.000														
Ca	0.112	0.003	0.238	1.000													
Cd	-0.275	0.024	-0.054	0.027	1.000												
Cr	-0.176	0.102	0.037	0.044	0.026	1.000											
Cu	0.010	-0.110	-0.069	0.218	-0.259	0.031	1.000										
K	-0.132	0.181	0.516	0.399	-0.155	0.455	-0.046	1.000									
Mg	-0.107	-0.039	0.609	0.407	-0.080	0.381	-0.067	0.499	1.000								
Mn	-0.337	-0.097	0.221	-0.459	0.215	0.278	0.180	0.101	0.135	1.000							
Mo	-0.088	0.087	-0.151	0.296	0.299	0.367	0.090	-0.198	0.158	0.023	1.000						
Na	0.252	-0.185	0.446	0.119	-0.333	0.395	0.096	0.540	-0.014	-0.100	-0.100	1.000					
Ni	-0.028	-0.172	0.162	0.419	-0.143	0.049	0.044	-0.031	0.208	-0.346	0.191	-0.086	1.000				
P	-0.263	0.219	0.004	0.144	-0.341	0.450	0.062	0.385	0.383	0.059	0.112	0.063	0.079	1.000			
Pb	-0.087	-0.004	-0.058	0.281	0.356	0.301	0.078	-0.211	0.138	0.039	0.960	-0.121	0.165	0.089	1.000		
Si	-0.160	0.331	0.376	0.555	-0.066	0.037	0.057	0.520	0.233	-0.248	-0.015	0.115	0.252	0.209	0.017	1.000	
Sr	-0.007	-0.365	0.761	0.200	-0.209	0.327	-0.117	0.629	0.739	0.311	-0.244	0.535	0.109	0.313	-0.227	0.179	1.000

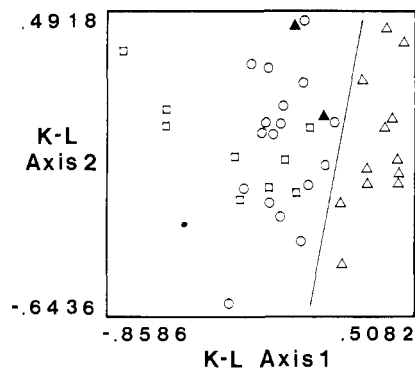


Figure 1. K-L projection of the entire data set from 17-dimensional space onto two-dimensional plot preserving 40% of total variance. France (Δ); Pacific Northwest (\circ); California (\square). Blackened symbols = misclassified samples.

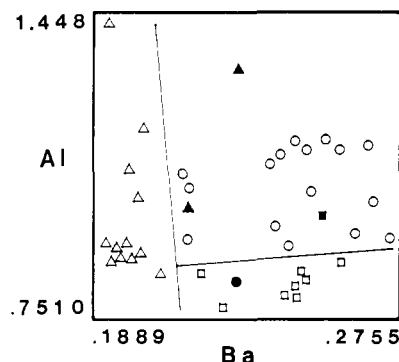


Figure 2. Plot of first SELECT feature "barium" vs. second SELECT feature "aluminum" for the classification of wine samples from France (Δ), Pacific Northwest (\circ), and California (\square). Blackened symbols = misclassified samples.

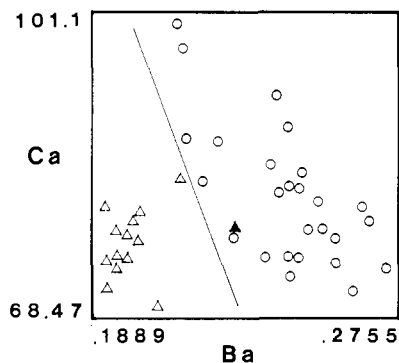


Figure 3. Plot of first SELECT feature "barium" vs. second SELECT feature "calcium" for the classification of wine samples from the United States (\circ) and France (Δ). Blackened symbols = misclassified samples.

the latter two regions from which French samples can be separated distinctly. One explanation is that so many of the Pinot Noir clones on the west coast of the United States have been derived from the same or closely related parent stock and none of the regions of the American wines match the soil types of the French areas. However, this separation is achieved when barium is plotted against aluminum, the first and second selected feature, respectively, for this classification. Figure 2, a plot of barium vs. aluminum, shows that there are four misclassifications with two French samples having a higher than average barium concentration, a Pacific Northwest sample having a low aluminum concentration, and the reverse for a California sample. Figure 3 is a plot of the first selected feature barium vs. the second selected feature calcium for

Table IV. SELECT, LEAST, KNN, and SIMCA Results for Six Classifications (US = United States, Fr = France, PNW = Pacific Northwest, Cal = California)

no. of data vector per category		US/Fr ^a	US/Fr ^b	PNW/Cal/Fr ^b	PNW/Fr ^b	Cal/Fr ^b	PNW/Cal ^b
		26/14	26/14	17/9/14	17/14	9/14	17/9
1st selected feature		Ba (6.084)	Ba (5.960)	Ba (3.514)	Sr (6.292)	Ba (7.966)	Al (3.552)
2nd selected feature		Ca (1.378)	Ca (1.375)	Al (1.883)	Ca (1.118)	Ni (1.233)	K (1.596)
3rd selected feature		Al (1.071)	Al (1.070)	K (1.531)	B (1.125)	B (1.058)	Ca (1.084)
17 features	LEAST	100%	100%	100% (PNW/Fr)	100%	100%	100%
	KNN ^c	98%	98%	100% (Fr/Cal)	97%	96%	85%
	SIMCA ^d	100%	100%	100%	96%	100%	100%
first selected feature	LEAST	95%	95%	94% (PNW/Fr) 57% (Fr/Cal)	97%	96%	92%

^a Experimental errors not included. ^b Experimental errors included. ^c Results of 1-PN. ^d Results of 1-component analysis.

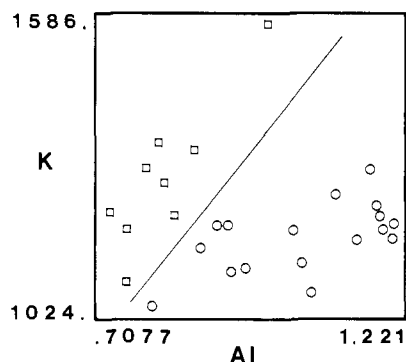


Figure 4. Plot of first SELECT feature "aluminum" vs. second SELECT feature "potassium" for classification of wine samples from Pacific Northwest (O) and California (□).

the separation of American and French Pinot Noir showing only one misclassification. Figure 4 is a similar display for separation between Pacific Northwest and California samples. This plot of aluminum vs. potassium gives a 100% correct classification.

These two-dimensional plots clearly demonstrate that successful classification can be achieved through visual display of data besides using mathematical methods such as LEAST. But information must first be obtained from feature selection as to which measurements are most important. Otherwise, examination of the data by the trial and error approach can be very inefficient and time consuming when the number of measurements involved becomes large.

Wine samples in this study were so selected as to allow, besides geographic classifications, investigations of intraregional as well as vintage variations. Although the number of samples used in each case might not be large enough to give a good statistical representation of the real situation, the data, nevertheless, provided some insights to these two factors.

Two different sets of data were used to study the intraregional variations. One set consisted of nine samples of vintage 1972 from French wineries and the other was composed of seven California samples of vintage 1973. Choosing samples from the same wine region for comparison reduces the effect that grape variety, climatic differences, and soil type within one region may have on elemental concentrations in the resulting wine to a minimum. Variations in elemental concentrations will then be mainly due to specific winemaking procedures such as type of yeast used and time and temperature of fermentation and storage, which generally vary among wineries. Concentrations of boron, barium, calcium, potassium, magnesium, manganese, and phosphorus are affected by these factors only to a small extent with relative standard deviations less than 30% in both California and French samples. On

the contrary, copper, sodium, and strontium concentrations vary greatly with relative standard deviations exceeding 50% in both regions. French samples, in particular, show marked differences in the level of strontium.

Twelve samples of vintages 1966–1974 from Associated Vintners in Washington were selected to illustrate vintage variations within a winery. Another set of four samples of vintages 1969–1972 from Givry, Domain Baron Therard in France were also chosen for the same purpose. In both vineyards, yearly variations show little effect on the concentrations of calcium, magnesium, manganese, phosphorus, and silicon in the wine produced with less than 30% relative standard deviations. Fluctuations in levels of cadmium, molybdenum, and lead are well over 60% relative standard deviations. Particularly large variations in copper and potassium concentrations, with 130 and 85% relative standard deviations, respectively, of different vintages from Associated Vintners are observed.

CONCLUSION

This study demonstrates the application of a combination of advanced instrumentation and sophisticated data analysis techniques to wine research. Atomic emission spectrometry with a relatively new plasma excitation source makes it possible to carry out multielemental analysis with sensitivity, reliability, and speed. Pattern recognition techniques enable useful information to be extracted from a massive amount of data. These techniques have been highly successful in this and previous studies undertaken by this laboratory. Taking advantage of these latest advances in analytical chemistry, wine analysis and other chemists working with complex mixtures will then have at their disposal, in addition to traditional techniques, a powerful tool for problem solving in their areas of research.

The importance of the inorganic components of wines to their stability and quality suggests that more should be learned about the interrelationships of the elemental concentrations and their effect on the sensory quality of wine. Research using a similar approach is in progress in our laboratory to take further advantage of the multivariate data analysis methods in pattern recognition and much more highly resolved organic component profiles of wine from glass-capillary chromatography. Interrelationships of elemental content, organic constituents, and sensory evaluations of wines of *Vitis vinifera* cv. Pinot Noir will be reported in future publications from this laboratory.

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A Comparison of Trace Element Contents of Florida and Brazil Orange Juice

James A. McHard,* Susan J. Foulk, and James D. Winefordner

A number of samples from Florida and Brazil orange juice concentrates have been compared as to their inorganic elemental content for the purpose of differentiating their geographical origin. Most of the elements tested were in similar concentration ranges in juice samples from the two geographical regions. A few, when compared as ratios to zinc as a reference element, showed geographic differences. The best elements for characterization purposes were found to be barium, boron, gallium, manganese, and rubidium.

The inorganic elemental content of orange juices and other plant products has been a subject of considerable interest and research activity since the relationship was established between some of these entities and plant, animal, and human nutrition. The monumental efforts of Henrik Lundegardh in the late 1930's and 1940's were the forerunner of much of the modern analytical interest. Lundegardh was the first to establish the utility of flame and spark spectrographic methods for soil and leaf analysis (Lundegardh, 1938, 1939, 1943; Hermann and Alkemade, 1963). Lundegardh's work showed the relationship of the soil content of major nutrients like calcium, phosphorus, and nitrogen and minor nutrients like manganese, copper, and iron to plant vigor and health. It has now been well established (Reitz et al., 1972) that these elements along with boron, magnesium, molybdenum, potassium, and zinc are essential elements in the promotion of satisfactory growth of orange trees and the production of fruit. All of these elements plus many more trace elements can be measured in orange juice relatively easily with equipment now commercially available.

Because of the important nutritive attributes of the 11 elements specifically listed above, most of the analytical effort in the past few decades has been directed toward the determination of the concentrations of these elements in foods and plants of interest. However, it is of more than just curiosity that gives inspiration to finding out what other elements are present. For example, there is a desire to know what toxic elements may be present and at what concentrations. Also, it is of interest to know if geographic locations affect the abundance of certain elements found in foods.

There have been only two comprehensive studies made on the elemental content of orange juices produced in the United States. The first of these was reported a little over 50 years ago by Roberts and Gaddum (1937) who compared the elements in several varieties of Florida oranges and grapefruit. These elements were measured spectrographically using a Littrow optical arrangement and a direct current arc source. Although not specifically stated in their publication it is presumed (because of the time period of the study) that the spectrograph was of the quartz prism design. Their compilation of results lists concentration estimates for 29 elements including carbon, oxygen, sulfur, and chlorine. The value of oxygen was calculated, but the authors did not indicate how the values for carbon, sulfur, and chlorine were obtained. Nine elements—bismuth, cadmium, cobalt, lead, molybdenum, nickel, silver, vanadium, and zirconium—were listed but either were not detectable or were declared as trace (detectable, but not measurable).

The only other comprehensive study was reported in the early sixties (Birdsall et al., 1961). Birdsall's study involved the measurement (among other things) of inorganic constituents in California lemons and oranges. This study was also carried spectrographically and included 31 elements, all of which were metals except boron and phosphorus. Of these 31 elements, eight [antimony, arsenic, bismuth, cadmium, cobalt, columbium (niobium), lead, and tungsten] were not detected and 12 were listed as trace (<0.01% of the ash).

Whereas the Roberts and Gaddum (1937) study gave concentration ranges (based on single strength orange juice) as narrow as a factor of 4, indicating an attempt to quantitation, the Birdsall study was only grossly proximate listing four classes: (1) those greater than 1% of the ash, (2) those between 0.01 and 1%, (3) those detectable but less than 0.01%, and (4) those not detectable.

* Department of Chemistry, University of Florida, Gainesville, Florida 32611.