

## LITERATURE CITED

- Amerine, M. A., *Adv. Food Res.* 8, 133-224 (1958).  
 Amerine, M. A., Berg, H. W., Cruess, W. V., "The Technology of Wine Making", Avi Publishing Co., Westport, CT, 1967, p 225.  
 Amerine, M. A., Joslyn, M. A., "Table Wine—The Technology of Their Production", University of California Press, Berkeley, CA, 1970, p 456.  
 Cover, T. M., Hart, P. E., *IEEE Trans. Inform. Theory* 13, 21 (1967).  
 Duewer, D. L., Koskinen, J. R., Kowalski, B. R., "ARTHUR" available from B. R. Kowalski, Laboratory for Chemometrics, Department of Chemistry, University of Washington, Seattle, WA 98195 (1976).  
 Harper, A. M., Duewer, D. L., Kowalski, B. R., Fasching, J. L., "ARTHUR and Experimental Data Analysis: The Heuristic Use of a Polyalgorithm", ACS Symposium No. 52, American Chemical Society, Washington, DC, 1977.  
 Jurs, P. C., Isenhour, T. L., "Chemical Applications of Pattern Recognition", Wiley-Interscience, New York, 1975.  
 Kowalski, B. R., *Anal. Chem.* 47, 1152A (1975).  
 Kowalski, B. R., Bender, C. F., *J. Am. Chem. Soc.* 94, 5632 (1972).  
 Kowalski, B. R., Bender, C. F., *J. Pattern Recogn.* 8, 1 (1976).  
 Kwan, W. O., Kowalski, B. R., *J. Food Sci.* 43, 1320 (1978).  
 McGill, J. R., Kowalski, B. R., *Appl. Spectrosc.* 31, 87 (1977).  
 Powers, J. J., Keith, E. S., *J. Food Sci.* 33, 207 (1968).  
 Wold, S., *J. Pattern Recogn.* 8, 127 (1976).  
 Wu, L. S., Bargmann, R. E., Powers, J. J., *J. Food Sci.* 42, 944 (1977).  
 Young, L. L., Bargmann, R. E., Powers, J. J., *J. Food Sci.* 35, 219 (1970).

Received for review January 31, 1979. Accepted June 11, 1979.

## 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.

Table I. Concentration Ranges of Various Elements in Parts per Million Based on Single Strength Orange Juice

element <sup>b</sup>	$\lambda$ , nm	Florida concn range, ppm	Brazil concn range, ppm	Florida ratio range <sup>a</sup>	Brazil ratio range <sup>a</sup>
Al	396.153	0.045-0.125	0.070-10.0	0.828-2.24	0.721-8.56
As*	234.984	<0.05			
Ba	455.404	0.025-0.070	0.185-0.750	0.783-2.96	5.15-24.9
Be*	234.861	<0.05			
Bi*	306.716	<0.05			
B	249.773	0.950-1.20	0.900-2.15	0.594-0.870	0.944-1.70
Ca	422.673	65-100	80-120	0.608-0.851	0.781-1.40
Cr	425.435	0.002-0.020	0.002-0.065	0.308-1.56	0.44-6.93
Co*	345.351	<0.01			
Cu	324.754	0.350-0.425	0.200-0.400	0.625-0.941	0.643-1.12
Ga	403.298	0.030-0.040	0.063-0.145	0.940-1.28	1.38-3.18
In	451.132	0.001-0.002	0-0.013	0.235-0.715	0-1.94
Fe	358.120	0.800-6.90	0.975-17.5	0.412-3.38	0.619-7.38
La	394.911	0.003-0.020	0-0.048	0.153-1.18	0-1.69
Pb	405.782	<0.15			
Li	670.781	0.001-0.002	0.002-0.005	0.306-0.63	0.560-21.4
Mg	285.213	95-120	130-170	0.795-1.00	0.281-1.47
Mn	403.307	0.250-0.315	0.450-0.800	0.86-1.06	1.382-3.25
Mo	379.825	0-0.003	0-0.005	0-2.15	0-3.82
Ni	341.477	0.010-0.025	0.008-0.090	0.409-1.47	0.368-1.39
P	214.911	120-155	155-310	0.674-1.06	0.0540-1.60
K	766.491	1500-1650	2030-2400	0.74-1.98	0.88-1.53
Rb	780.023	0.365-0.740	2.65-6.48	0.693-1.85	6.05-11.5
Sc	361.384	0-0.001	0-0.003	0.0236-0.220	0.0104-5.93
Ag	328.068	<0.001	0.001-0.035		0.0980-1.58
Na	588.995	1.85-4.30	1.50-25.5	0.425-1.013	0.0453-7.07
Sr	460.733	0.095-0.980	0.290-1.10	0.199-1.670	0.265-2.02
Sn	303.412	0-0.420	0.015-2.58	0-2.60	0.330-52.11
Ti	334.941	0.005-0.020	0.015-0.350	0.437-1.46	0.782-28.7
V*	437.924	0.01			
Y*	412.831	<0.1			
Zn	213.856	0.350-0.450	0.250-0.425		

<sup>a</sup> The ranges of the ratios of the concentrations of the elements as described in the text:  $(I_{AY}/I_{ZnY})/(I_{AR}/I_{ZnR})$ . <sup>b</sup> Asterisk indicates concentration was below the detection limit.

In an attempt to update these studies and especially to measure the differences, if any, between the trace mineral constituents of Florida juices and those of Brazil juices, the study reported here was undertaken. Originally, 32 elements were selected for study as shown in Table I. However, six of these (marked with an asterisk) were eventually eliminated from consideration because they were consistently too low in concentration to obtain useful measurements.

#### EXPERIMENTAL SECTION

Eight commercial brands of Florida orange juice were selected for study. These were the same brands selected for the atomic absorption study reported by the authors in a previous publication (McHard et al., 1976). The samples of these brands were purchased at food markets in the early spring of 1977. For comparison, 42 samples of Brazilian juices imported during the fall of 1978 were supplied to us by the U.S. Department of Agriculture Processed Foods Inspection Service at Winter Haven, Florida. All samples were prepared for analysis by dry ashing. Twenty-gram samples of frozen orange juice concentrate were dried to carbonization under heat lamps and ashed until the ash residue was completely free of any visible unoxidized carbon. The ashing was accomplished in a muffle furnace at 550 °C for ~16 h (Horwitz, 1970). The final ash was dissolved in 0.1 M HNO<sub>3</sub> (50 mL) and analyzed by plasma spectroscopy. The spectrometer was the Spectrametrics, Inc. Spectraspan II equipped with the Spectrajert III Plasma source. The wavelengths used for each element are listed in Table I. Generally for each individual measurement, two readings (15-s integration time) were averaged and compared to a standard containing the element being determined in a suitable matrix. A recent publication by the authors (McHard et al., 1979) discusses

the matrix and matrix effects on the analysis.

#### RESULTS AND DISCUSSION

In Table I the concentration ranges of the elements in the juices from Florida and Brazil are listed. These concentration ranges, for many elements, show considerable overlap when comparing the two geographical regions. However, close examination shows that the ranges for a few elements are significantly different. In order for meaningful comparisons to be made, the elemental results must be compared on an equal solids basis. The soluble solids content of the Brazilian concentrates was, in most instances about 60° Brix compared to 45° Brix for the Florida concentrates. One way to eliminate the effect of differences of soluble solids content between the samples without resorting to specific gravity measurements is to use elemental ratios, especially if an element can be found which has a particularly uniform concentration in juices from both sources. An examination of the results showed that the values for zinc in the samples from the two sources were remarkably uniform throughout. On the basis of this finding, a ratio of elements was arrived at that eliminated the need for taking solids content of the samples into account. It also turned out that this ratio was a quite sensitive parameter for comparing the juices from the two sources. For calculation of the ratio, along with choosing zinc as the reference element, one of the Florida brands was selected as a reference sample. The methodology of ratioing the reference element Zn to the element being determined and the method of application of the ratio to eliminate the solids factor is described in the Appendix. Thus the ratio used is  $(I_{AY}/I_{AR})/(I_{BY}/I_{BR})$ , where A is the element under consideration, B is the reference element (in this case zinc), *I* is the intensity reading for the respective element, Y is the sample being analyzed, and R

Table II. Ratios<sup>a</sup> of Selected Elements and Deviations Shown by Brazil Samples Compared to Florida Samples as a Standard Reference Population

element	Florida			Brazil		
	range	$\bar{x}$	SD	range	dev ( $\alpha$ )	$P^b$
Ba	0.7833-2.9661	1.5115	0.7468	5.1570-24.8913	4.8815-31.1727	$(4.1966 \times 10^{-2})-(1.029 \times 10^{-3})$
B	0.5938-0.8792	0.7831	0.0980	0.9448-1.6979	1.6500-13.6031	$(3.6731 \times 10^{-2})-(5.4041 \times 10^{-3})$
Ga	0.9403-1.2812	1.0296	0.1121	1.3794-3.1828	3.1204-19.2079	$(1.0270 \times 10^{-1})-(2.7104 \times 10^{-3})$
Mn	0.8597-1.0586	0.9563	0.0732	1.3916-3.2465	5.9467-31.2869	$(2.8278 \times 10^{-2})-(1.0216 \times 10^{-3})$
Rb	0.6928-1.8473	1.1386	0.4117	6.0511-11.4510	11.9322-25.0483	$(7.0236 \times 10^{-3})-(1.5938 \times 10^{-3})$

<sup>a</sup>  $(I_{AY}/I_{ZnY})/(I_{AR}/I_{ZnR})$ . <sup>b</sup> Tschebycheff's inequality:  $P(|x - \bar{x}|) > \alpha s < (1/\alpha^2)$ .

is the reference sample (one of the Florida brands chosen for this purpose). The concentration ranges of the elements and the respective ratios calculated using the above formula are shown in Table I.

Examination of these results reveals that five elements show significant differences between the ratio ranges for samples from the two regions (Table II). Although other elements, for example, silver, might appear to be useful also, the wide range in concentration shown in the Brazil samples is too great and the low end of the range is too near the detection limit to allow any degree of confidence in assessing differences. The reason for the marked differences in the concentrations of elements like barium and rubidium are not clearly understood, but since these elements are not used as fertilizers or plant disease control agents it would seem that soil differences must account for the disparity in values.

One prime objective of this study was to be able to arrive at a probability of determining the origin of a sample by analyzing a sample of unknown source (in this case either Florida or Brazil) and by using the ratios described above. The Florida group of samples was selected as the standard population (the population of reference). Thus an average  $\bar{x}$  for each of the five elements was calculated for the Florida group and is listed in Table II along with the corresponding standard deviation. Under the set of columns labeled Brazil are listed the ranges of elements ratios of the Brazil samples and the ranges of deviations ( $\alpha$ ) of these samples. In the last column is shown  $P$  which is calculated using Tschebycheff's inequality (Nalimov, 1963; Kaiser, 1970)  $P(|x - \bar{x}|) > \alpha s < (1/\alpha^2)$ , where  $P$  is the probability that the sample tested is from Florida,  $x$  is the sample value,  $\bar{x}$  is standard population average,  $s$  is the standard deviation of the values of the reference population, and  $\alpha$  is the number of standard deviations represented by  $|x - \bar{x}|$  for the unknown sample. The element of the list of five that is most selective is rubidium and the element of least selectivity is gallium.

Since it can be assumed that the occurrence of any element is an independent event (not related to the presence of any of the others), one could calculate a combined probability  $P_{Ba} \times P_B \times P_{Ga} \times P_{Mn} \times P_{Rb}$ . This would give total probabilities in the order of  $10^{-5}$  or less. Thus it appears likely that with the use of these combined probabilities a sound decision could be made regarding a sample's origin.

#### SUMMARY

Results of the analysis of 32 elements in Florida and Brazil frozen concentrated orange juice samples have been presented. It is shown that using probability statistics, one can use the relative occurrence of five elements as ratios

to zinc as "fingerprint" indicators of the geographic source of a sample.

#### APPENDIX

- (1)  $I_{AY}$  = analyte signal for element A in sample Y.
- (2)  $I_{AR}$  = analyte signal for element A in reference R.
- (3)  $K_A$  = factor to convert intensity of signal for element A to weight of A.
- (4)  $W_Y$  = weight of sample Y.
- (5)  $K_Y$  = factor to convert weight of sample Y to weight of solids in sample Y.
- (6)  $(I_{AY}K_A)/(W_YK_Y)$  = weight of element A in sample Y solids.
- (7)  $(I_{BY}K_B)/(W_YK_Y)$  = weight of element B in sample Y solids.
- (8)  $(I_{AR}K_A)/(W_RK_R)$  = weight of element A in reference solids.
- (9)  $(I_{BR}K_B)/(W_RK_R)$  = weight of element B in reference solids.

$$\frac{(6)}{(8)} \div \frac{(7)}{(9)} = \frac{I_{AY}}{I_{AR}} \div \frac{I_{BY}}{I_{BR}}$$

$$\frac{(6)}{(8)} \div \frac{(7)}{(9)} = \frac{I_{AY}}{I_{AR}} \div \frac{I_{BY}}{I_{BR}}$$

#### LITERATURE CITED

- Birdsall, J. J., Derse, P. H., Tepley, L. J., *J. Am. Diet. Assoc.* **38**, 555-9 (1961).
- Hermann, R., Alremade, C. T. J., "Chemical Analysis by Flame Photometry", 2nd ed, Interscience, New York, 1963, Chapter 5.
- Horwitz, W., Ed., "Official Methods of Analysis", Association of Official Analytical Chemists, Washington, DC, 1970.
- Kaiser, H., *Anal. Chem.* **42**, 40A (1970).
- Lundegardh, H., *Soil Sci.* **45**, 447-54 (1938).
- Lundegardh, H., *K. Lantsbruksakad. Ted.* **78**, 157 (1939).
- Lundegardh, H., *Nature (London)* **151**, 310, 11 (1943).
- McHard, J. A., Foulk, S. J., Nikdel, S., Ullman, A. H., Pollard, B. D., Winefordner, J. D., *Anal. Chem.*, **51**, 1613-1616 (1979).
- McHard, J. A., Winefordner, J. D., Ting, Sik-Vuk, *J. Agric. Food Chem.* **24**, 950-953 (1976).
- Nalimov, V. V., "The Application of Mathematical Statistics to Chemical Analysis", Addison-Wesley, Reading, MA, 1963, Chapter VI.
- Reitz, H. J., Leonard, C. D., Stewart, I., Koo, R. C. J., Calvert, D. V., Anderson, C. A., Reese, R. L., Smith, P. F., "Recommended Fertilizer and Nutritional Sprays for Citrus", Bulletin, Institute for Food and Agricultural Sciences, University of Florida, Bulletin 536e, Dec 1972.
- Roberts, J. A., Gaddum, L. W., *Ind. Eng. Chem.* **29**, 574-5 (1937).

Received for review June 20, 1979. Accepted August 15, 1979. This research was supported by the Department of Citrus and in part by AFOSR-F44620-76-C-0005.