

the library of compounds used for identification. Fig. 5 and Fig. 6 compare the quality of the mass spectrum of ethyl butyrate as obtained from the system with the Grob injector, J&W OCI injector and the data system library entry. The sample spectra are from the same sample and analyzed on the same column. The small differences in the spectra are vital when determining isomers such as carvone (Fig. 7) or terpenes (Fig. 8).

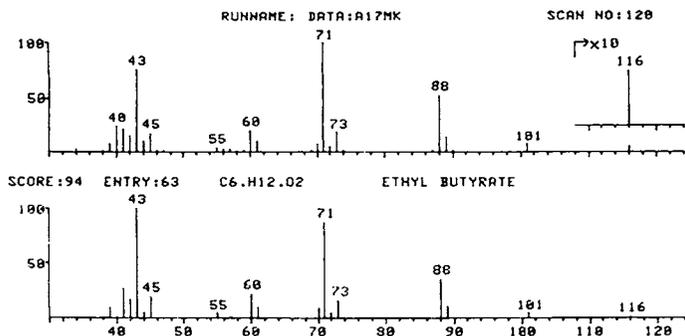


Fig. 6. Mass spectrum of ethyl butyrate compared with data system entry. Sample was analyzed with the J&W OCI injector and 30 m DB-1 column. The reduced chemical background results in a much higher match score.

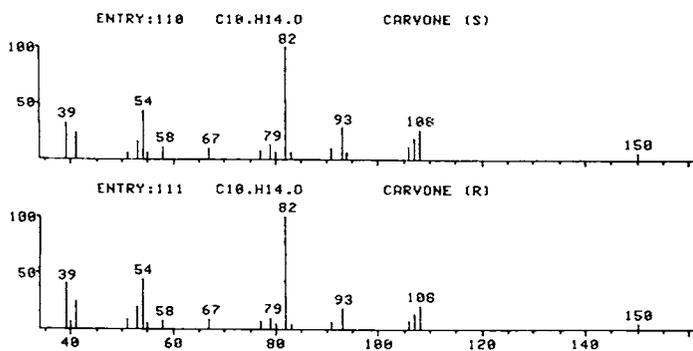


Fig. 7. Comparison of library entries of isomers of carvone. The intensity ratios of the masses are nearly identical. Successful identification of isomers depends heavily upon minimal artifact production which changes the intensity ratio of the resolved component in a gc analysis.

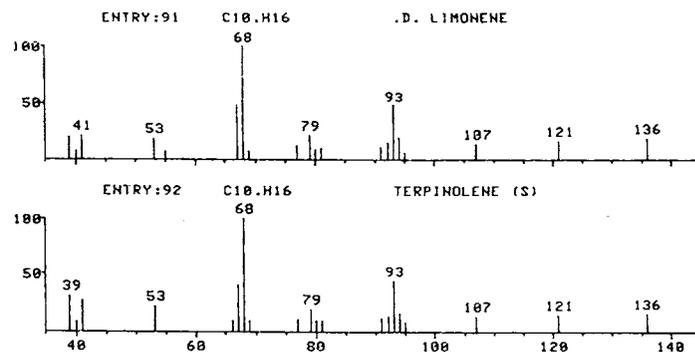


Fig. 8. Comparison of library entries of two common terpenes. The intensity ratio of masses 39 and 41 and the presence or absence of mass 66 are vital for correct identification. Artifact production with the Grob injector adds to these masses resulting in an inability to provide positive identification.

### Summary

The cold on-column injection technique has clearly demonstrated its superiority when used in a gc-ms system for analysis of aqueous essence samples. The mechanical design of the injector tested provides simple retrofit installation on any gas chromatograph that is using fused silica capillary columns of 0.32 mm id or smaller. The reduced temperatures that the sample is subjected to lowers the probability that artifact production occurs. The elimination of steam passing through the column should result in extended column life. Further improvements in sensitivity and dynamic range of the detector used are needed to fully utilize the potential of cold on-column injection techniques.

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## CITRUS JUICE TRACE METAL ANALYSIS BY AUTOMATED SEQUENTIAL MULTIELEMENT ICAP-AES

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*Additional index words.* atomic emission spectrometry, inductively coupled argon plasma, minerals in orange and grapefruit juices.

*Abstract.* Major (P, Mg, Ca, K, Na), minor (Ba, B, Mn, Mo, Ni, Zn, Cu, Al, Fe, Sr, Rb) and ultra trace elements (Sn, Co, Cr, Ti, V, Li) in frozen concentrated orange juice (FCOJ) and canned single-strength grapefruit juice (SSGJ) were determined by an automated fast sequential multielement

spectrometer combined with Inductively Coupled Argon Plasma (ICAP) Atomic Emission Spectrometry (AES). The mean values for Ba, B, Rb, and Ti in canned SSGJ were lower than in the commercial FCOJ. Also, canned SSGJ mean values for P, K, Mn, and Li were lower than in FCOJ samples prepared at the Citrus Research and Education Center (CREC). All the other elements of canned SSGJ mean values were higher than the FCOJ. The mean value for Sn in canned SSGJ was significantly higher than in the CREC and commercial FCOJ samples.

There have been relatively few references on the comparison of trace metals in orange and grapefruit juices. Roberts and Gaddum (6) reported the elemental concentrations for several cultivars of Florida oranges and grapefruit in 1937. McHard et al. (1) compared some modern approaches to orange juice analysis in a recent

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publication, and there were various definitions to describe the concentration range of a particular element.

Orange and grapefruit juices are major products of the Florida citrus industry. Our current interest is to measure mineral contents of SSOJ and SSGJ processed in Florida.

In this paper, we will consider the following terminology for trace minerals in citrus juices; major trace, minor trace, and ultra trace. This terminology is purely arbitrary and is not meant to be offered for adoption. Reitz et al. (5) reported that B, Ca, Cu, Fe, K, Mg, Mn, Mo, P, and Zn are essential elements in the promotion of satisfactory growth of citrus trees and the production of fruit. Also, it is known that Ca, Cu, Fe, K, Mg, Na, P, and Zn are essential elements in human nutrition (9).

### Materials and Methods

*Standard materials.* All chemicals used to prepare standard solutions were certified pure from Spex Industries. Reference solutions were prepared by dissolving the metals or their pure salts in a matrix to simulate citrus juice mineral constituents.

Trace elements at levels of part per billion (ng/ml) range were made in 0.1 M double distilled nitric acid solution. Also, the matrix contained 2400 µg/ml of K, 300 µg/ml of P, 150 µg/ml each of Ca and Mg, and 80 µg/ml of Na. This matrix was used to study the mineral contents of orange and grapefruit juices. For unknown samples, the elemental concentrations were calculated on the basis of micrograms of each element per gram of sample. Also, all concentrations were computed based on 11.8° Brix.

*Sample collection and preparation.* Samples of commercial FCOJ and canned SSGJ were collected on a bi-weekly basis from each of the participating processing plants in Florida by the U.S.D.A. processed food division supervising inspectors and by Department of Citrus personnel. Commercial FCOJ samples were reconstituted to single-strength orange juice (SSOJ) and transferred to glass bottles. All samples of SSOJ and SSGJ were stored at -10°C. FCOJ samples of CREC were processed in the Lake Alfred pilot plant, and stored in drum containers with a plastic bag inside to prevent juice contact with the metal. 'Hamlin', 'Pineapple' and 'Valencia' FCOJ samples from CREC were reconstituted to SSOJ, and then transferred to the glass bottles and stored at -10°C. Three samples were randomly selected from each plant and they were analyzed for 22 elements.

To prepare samples for analyses, 20 g of SSOJ were weighed in platinum crucibles and mixed with 2 ml of 0.5 M nitric acid; they were evaporated at 80°C in a muffle furnace for 3 hr and then ashed at 500°C for another 8 hr.

The remaining white residue was dissolved in 5 ml of 0.5 M nitric acid, the solution was transferred to a volumetric flask, washed and diluted to a total volume of 25 ml.

*Plasma emission spectrometry.* Spectrochemical analysis was carried out on a Jarrel-Ash Atomscan 2000 sequential, computer controlled multielement spectrometer equipped with an autosampler. The operating conditions for the instrument are shown in Table 1.

The analytical line selection was based on values given in the literature and on an experimental investigation of the spectral proximity using the spectrometer scanning system. Spectral lines used in this work are given in Table 2.

### Results and Discussion

The 22 elements measured in each sample, are grouped as major trace (concentration greater than 1 ppm), minor trace (concentration range 0.1-1 ppm), and ultra-trace ele-

Table 1. Operating parameters for ICAP-AES.

Parameter description	Condition I (Group Ia)	Condition II (All other)
Source gas	argon	argon
Gas flows:		
Sample	0.6 liters/min	0.45 liters/min
Aux.	0 liters/min	0 liters/min
Plasma	17 liters/min	17 liters/min
Power	0.75 kW	1.25 kW
Obs. height	11 mm	16 mm
PMT:	R427, R300, and R889	
Nubulizer	Modified cross-flow (JARRELL-ASH)	
Sample uptake		
Rate (ml/min)	1	1
Resolution:	.018 nm for 178-380 nm	
	.036 nm for 380-780 nm	

Table 2. Spectral lines used for analysis.

Element	Symbol	Wavelength (nm)
Phosphorus	P	214.91
Magnesium	Mg	279.08
Calcium	Ca	422.67
Potassium	K	769.90
Sodium	Na	589.59
Barium	Ba	455.40
Boron	B	249.77
Manganese	Mn	257.61
Molybdenum	Mo	203.84
Nickel	Ni	221.65
Zinc	Zn	213.86
Copper	Cu	324.75
Aluminum	Al	237.34
Iron	Fe	238.20
Strontium	Sr	407.77
Rubidium	Rb	780.02
Tin	Sn	235.48
Cobalt	Co	228.62
Chromium	Cr	205.55
Titanium	Ti	334.94
Vanadium	V	292.40
Lithium	Li	670.78

ments (concentration less than 0.1 ppm). The mean, the standard deviation (SD), and range of concentration for 22 elements in FCOJ authentic samples of CREC, commercially processed FCOJ, and canned SSGJ for the 1983-84 season, are shown in Tables 3, 4, and 5. Nagy (3) and Ting (8) stated that the high levels of certain elements (e.g., Na, P) in citrus juices may have been due to processing conditions rather than to normal levels for these elements in fruits.

Potassium is the most abundant element in orange and grapefruit juices. The mean values of K and P in orange juice samples from CREC are higher than in the commercial orange and grapefruit juices.

In contrast, the mean values of Ca and Na are lower in samples from CREC than in the commercial orange and grapefruit juices. Grapefruit juices have higher Mg contents than orange juices. The mean values of major trace elements in canned SSGJ are higher than in the orange juices processed commercially.

McHard et al. (2) have shown that certain elements in the minor trace group of elements have significantly different concentrations when they compared Florida SSOJ with orange juices from Brazil, Mexico, and California. Comparing the mean values of minor trace elements in Table 3 and Table 4, one can observe that Cu, Fe, Mn, and Zn have higher values in CREC samples. The mean values of B, Ba,

Table 3. Mineral constituents of Citrus Research and Education Center orange juice.

Element	Mean (µg/g)	SD	Range
P	174.1	17.4	149.5 -197.1
Mg	125.2	18.5	97.43 -139.3
Ca	87.51	10.0	70.58 -100.8
K	1856.0	173.0	1666. -2039.0
Na	2.048	0.736	1.061 -3.034
Ba	0.0306	0.013	0.0163-0.0465
B	0.9913	0.303	0.6623-1.603
Mn	0.3056	0.034	0.2596-0.3459
Mo	0.1995	0.160	0.0021-0.4451
Ni	0.2989	0.079	0.2256-0.4161
Zn	0.3879	0.072	0.2794-0.4863
Cu	0.2798	0.139	0.1177-0.5589
Al	0.2265	0.042	0.1742-0.3021
Fe	0.8595	0.113	0.7225-1.041
Sr	0.1578	0.017	0.1412-0.1828
Rb	0.1839	0.043	0.1478-0.2656
Sn	0.0121	—	LOD <sup>a</sup>
Co	0.0012	—	LOD
V	0.0022	—	LOD
Cr	0.0598	0.053	0.0021-0.1315
Ti	0.0734	0.129	0.0032-0.3508
Li	0.0082	0.004	0.0006-0.0128

<sup>a</sup>Limit of determination.

Table 4. Mineral constituents of commercially processed orange juice from Florida.

Element	Mean (µg/g)	SD	Range
P	156.1	16.4	135.3 -199.3
Mg	112.6	15.5	90.85 -143.4
Ca	111.0	25.5	63.40 -174.8
K	1531.0	215.0	1237. -2140.0
Na	6.813	2.98	3.330 -15.23
Ba	0.2822	0.223	0.0194-0.7425
B	1.218	0.322	0.8374-1.838
Mn	0.2118	0.047	0.1494-0.3159
Mo	0.5731	0.290	0.0847-1.365
Ni	1.113	0.929	0.3621-4.645
Zn	0.3502	0.343	0.1295-1.709
Cu	0.1939	0.110	0.0452-0.4260
Al	0.2580	0.089	0.0539-0.4148
Fe	0.6949	0.239	0.1200-1.102
Sr	0.7257	0.386	0.0837-1.720
Rb	0.4630	0.326	0.1495-1.572
Sn	0.0971	0.079	0.0121-0.3045
Co	0.0049	0.005	0.0012-0.0159
V	0.0187	0.007	0.0022-0.0279
Cr	0.0651	0.017	0.0351-0.0933
Ti	0.0147	0.014	0.0032-0.0650
Li	0.0021	0.001	0.0010-0.0062

Fe, and Sr in canned SSGJ are higher than in the CREC samples of FCOJ. Nagy et al. (4) and Smoot and Nagy (7) have given the explanation and possible mechanism of detinning in canned orange and grapefruit juices. The mean value of Sn in canned SSGJ is significantly higher than in the orange juices.

### Conclusion

The most abundant element in SSOJ and SSGJ is K

Table 5. Mineral constituents of processed grapefruit juice from Florida.

Element	Mean (µg/g)	SD	Range
P	164.1	10.9	132.2 -180.6
Mg	133.0	13.9	106.1 -154.2
Ca	126.7	30.3	87.92 -195.2
K	1682.	380.0	790.2 -2285.0
Na	9.150	5.41	3.030 -24.94
Ba	0.1807	0.117	0.0560-0.4443
B	0.9391	0.219	0.5896-1.508
Mn	0.2285	0.097	0.1446-0.7200
Mo	0.6688	0.398	0.2627-1.920
Ni	1.612	1.08	0.4445-3.926
Zn	0.6544	0.613	0.2890-3.335
Cu	0.3678	0.187	0.1215-0.9616
Al	0.5560	0.580	0.0265-2.692
Fe	1.416	1.52	0.0283-6.940
Sr	0.8345	0.544	0.2747-2.476
Rb	0.2311	0.094	0.0510-0.4916
Sn	0.5664	0.517	0.0121-2.252
Co	0.0080	0.007	0.0012-0.0228
V	0.0273	0.015	0.0022-0.0626
Cr	0.1052	0.024	0.0400-0.1670
Ti	0.0098	0.006	0.0032-0.0212
Li	0.0025	0.001	0.0010-0.0046

with average values of 1856, 1531, and 1682 ppm for CREC, reconstituted FCOJ, and canned SSGJ, respectively. Comparison of orange and grapefruit juices from commercial sources showed significant differences in average concentrations of Sn, Rb, Fe, and Al. The range of concentrations for Ca, K, Na, Ba, Ni, Zn, Cu, Al, Fe, Sr, and Rb are wider in commercial SSOJ and SSGJ than CREC samples of SSOJ. These differences are considered to be due to growing conditions and processing operation.

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