The analysis of trace metals in fruit, juice, and juice products using a
DUAL-VIEW PLASMA

Karen W. Barnes
PerkinElmer Instruments, 761 Main Avenue, Norwalk, CT 06859-0215 USA

Introduction

The issue of food analysis is exceedingly complex and requires the cooperative efforts of knowledgeable, dedicated individuals from many disciplines. Understanding the implications of metals in foods seems deceptively simple; however, this is not the case. Metal determinations can resolve many issues and are typically performed to answer three questions. First, how much of a nutrient metal (mineral) is present and is the product labeled properly? Next, is the product what it claims to be and does it comply with trade laws? Finally, is the product wholesome and safe to eat, is it contaminated, or has it been tampered with? A discussion of the major issues and how these questions may be answered using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) follows.

Food Labeling and Nutrient Mineral Content

The issue of nutrient labeling has come to the forefront because of the Nutrition and Labeling Education Act of 1990 (NLEA) that was passed to help consumers maintain healthy dietary practices. Former food labeling requirements were somewhat lenient and required nutritional labeling only if a product made specific or implied health claims.

Table 1: The Nutrition Labeling Education Act of 1990 Food Labeling Requirements

Mandatory Nutrients	Voluntary Nutrients		
Calories	Calories from Saturated Fat	Vitamin K	Copper
Calories from Fat	Calories from Unsaturated Fat	Thiamin	Manganese
Total Fat	Calories from Carbohydrates	Riboflavin	Fluoride
Saturated Fat	Calories from Protein	Niacin	Chromium
Cholesterol	Unsaturated Fat	Vitamin B6	Molybdenum
Sodium	Polyunsaturated Fat	Folate	Chloride
Total Carbohydrates	Monounsaturated Fat	Vitamin B12	
Total Sugars	Sugar Alcohols	Biotin	
Dietary Fiber	Soluble Fiber	Pantothenic Acid	
Protein	Insoluble Fiber	Phosphorus	
Vitamin A	Protein as %	Magnesium	
Vitamin C	Potassium	Zinc	
Calcium	Vitamin D	Iodine	
Iron	Vitamin E	Selenium	

NLEA required full nutritional labeling of 14 mandatory nutrients for most Food and Drug Administration (FDA) regulated packaged food products. Calcium, iron, and sodium are mandatory nutrients. Thirty-five other nutrients, including nine additional metals, may be labeled voluntarily. It has been predicted that these nutrients will become mandatory in the near future (1). Very few foods are exempt and the complete NLEA regulations were published in the Federal Register (2). It was estimated that 17,000 food companies in the United States were affected by NLEA and that labels for ≈200,000 products required modification (2). Costs to implement NLEA were projected at $2 billion (3). Food labeling requirements are listed in Table 1.

PerkinElmer™
instruments.

The analysis of metals in foods is challenging due to the high variation in levels present. The situation is complicated by naturally occurring seasonal and varietal variations. The use of official validated analytical methodology is preferred by regulatory agencies; however, many official methods are analyte- and matrix-specific. A review of current validated Association of Official Analytical Chemists International (AOAC) methodology for minerals and metals in foods (4) revealed that many single-element methods are currently in use. These methods include titrations, colorimetric analyses, UV/Visible analyses, and flame and graphite furnace atomic absorption spectroscopy. Many of the methods have sample throughput constraints and relatively narrow linear dynamic ranges. Others require the use of solvents banned by the Montreal Protocol on Substances that Deplete the Ozone Layer (5). Time constraints make multiple sample dilutions and independent analysis impractical and limit the utility of some methods. AOAC recognized the need for improved methodology and developed a tool to help analysts develop rugged generic methods. The Food Matrix Triangle (6) categorizes foods into nine sectors based on fat, carbohydrate, and protein content. AOAC proposes that a method can be tested for all food matrices by analyzing eighteen types of samples, two from each sector. The Food Matrix Triangle is presented in Figure 1. Although no AOAC food methods currently employ ICP-OES, the multielement capability, wide linear dynamic range, and high sample throughput are attributes that will prove beneficial to analysts striving to meet the challenges created by NLEA.
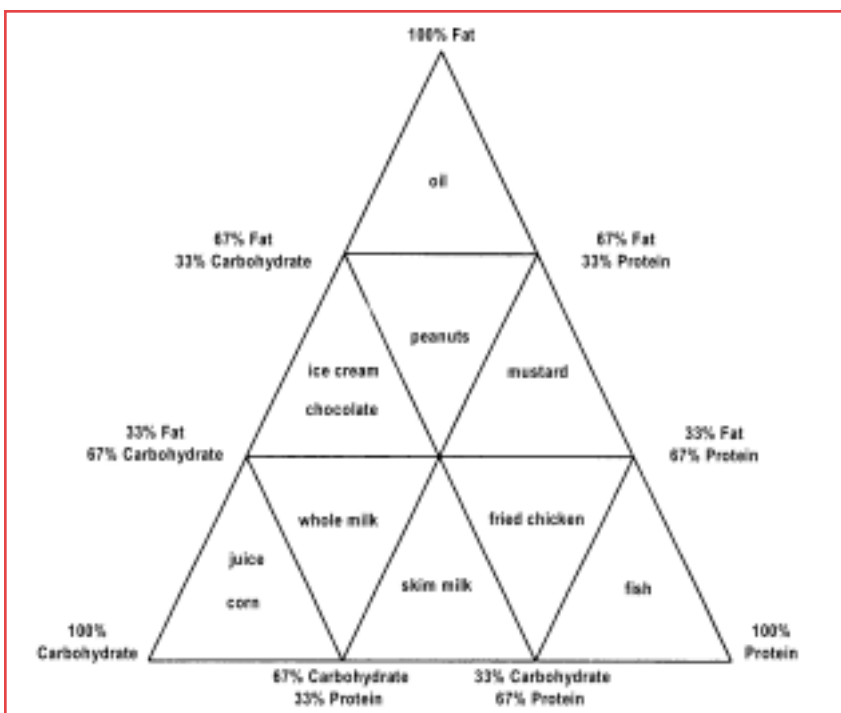

Figure 1. Food Matrix Triangle.
(Reprinted from The Referee, Volume 17, Number 7, Pages 6-7, 1993.)

Is the Product What it Claims to be and Does it Comply With Trade Laws?

This question encompasses the issues of adulteration and misbranding. Misbranding refers to misleading or inappropriate labeling, and is directly linked to NLEA. It was included in this discussion however, because it is related to another issue, adulteration. Adulteration encompasses two areas, contamination and fraud involving the deliberate substitution of a less valuable constituent in a food (7-8). Often an adulterated product is also misbranded. Trace metal analyses may detect occurrences of both. For example, a vegetable labeled "low salt" would be misbranded if the sodium levels in the product were higher than claimed on the label. Valuable constituents omitted from foods may have mineral profiles that can identify the adulteration. For example, a juice "cut" with water, sugar, and flavors might have a lower calcium content than 100% pure juice. Misbranding and adulteration issues occasionally involve the geographical origin of products. For example, a product sold as 100% pure Florida orange juice would be misbranded and adulterated if juice from another area was blended in. Trace metal profiles have been used to establish the country of origin of foods because plants often have an "elemental fingerprint" that matches that of the soil in which they grew. Plants grown in different locations may have different elemental profiles. Orange juice (9), macadamia nuts and pistachios (10) have been characterized in the literature.

Food Quality and Safety

This complex question addresses many areas including food quality, adulteration, tampering, contamination, environmental pollution, and geographical origin. Metal determinations can be pertinent to all and examples will be discussed briefly. A classic example of the application of ICP-OES to determine the food quality involves food grade oils. Oils contaminated with ppb levels of metals can undergo accelerated oxidation, and foods incorporating these oils may taste rancid. Sample preparation is difficult and involves the use of flammable solvents. Lack of analytical sensitivity restricts the choice of usable analytical techniques. The utility of ICP-OES for oil analysis has been demonstrated (11).

Tampering, is a form of adulteration and refers to deliberate criminal acts. Components deliberately added to food may have characteristic metal profiles that can link occurrences of tampering. Contamination from food packaging is also becoming more of an issue. To protect children, the U.S. FDA recently reduced the allowable lead levels in foods packaged in lead-soldered cans (7). This was implemented following a 1992 incident in which an 18 month-old child was found to have elevated blood lead levels caused by drinking juice from lead-soldered cans. The child drank approximately 36 ounces of juice daily and ingested 600 μg of lead daily; a level sufficiently high enough to effect permanent damage and disability to the child. Should lead analysis become mandatory, ICP-OES would be an applicable technique. The environment in which a food is grown can also cause contamination. For example, plants grown in contaminated soil and fish from polluted waters may be contaminated with heavy metals that can be monitored with ICP-OES.

Advantages of ICP-OES

Although few food analysts currently employ ICP-OES, the multielement capability, wide linear dynamic range, and high sample throughput are attributes that will prove beneficial to analysts striving to perform these determinations. An axially viewed plasma provides increased sensitivity, lower background, and improved detection limits compared to a traditional, radially viewed plasma. Viewing a plasma axially extends the source path length, thereby increasing analyte emission intensity and improving sensitivity. This sensitivity enhancement results in a 5- to 10-fold improvement in detection limits over radially viewed plasmas. With this configuration, elements can be determined at levels previously only attainable with GFAAS. A comparison of detection limits by technique is presented in Table 2 (12). Radial viewing of a plasma offers advantages of higher upper limit of linearity, reduced easily ionizable element effects, lower physical interferences, and fewer spectral

Table 2: Detection Limits (3σ) in μg/L (ppb) as a Function of Analytical Technique

| Element | ICP | | GFAAS |
	OPTIMA 3000 XL	Plasma 2000	5100 ZL
Ag	0.4	1.5	0.05
Al	2	6	0.3
As	2	30	0.5
Ba	0.07	0.15	0.9
Be	0.08	0.09	0.02
Cd	0.2	1.5	0.02
Co	0.4	3	0.4
Cr	0.2	3	0.08
Cu	0.5	1.5	0.25
Fe	0.3	1.5	0.3
Hg	0.5	30	1.50
K	2	75	0.02
Mn	0.1	0.6	0.09
Mo	0.7	7.5	0.2
Na	3	6	0.05
Ni	0.7	6	0.8
Pb	0.8	30	0.15
Sb	2	90	0.4
Se	2	90	0.7
Sr	0.1	0.08	0.06
Ti	0.2	0.75	0.9
Tl	2	60	0.4
V	0.4	3	0.3
Zn	0.1	1.5	0.3

interferences. A dual-view plasma offers the best of both worlds. High analytical sensitivity for minor components and extended linear dynamic range sufficient to allow the accurate determination of major components.

The objective of this study was to determine concentrations of trace metals of interest for nutritional labeling, geographical origin, tampering, and contamination in fresh fruit, juice, and juice products using a dual view plasma. Major components were determined using the plasma in the radial configuration and minor components were determined using the axial configuration. Matrix-matching of elemental and acid composition was performed to minimize spectral and physical interferences. By appropriate sample dilution, major components were also determined using the axial view to permit comparison with and to validate the radial view results.

Experimental
Juice Sample Preparation
Samples of authentic juices were prepared from the raw fruit and diluted to single strength and analyzed in this study. Three subsamples of each product were prepared by microwave digestion using a MDS 2100 microwave system (CEM, Matthews, NC). Each juice was well shaken, opened and sampled by pouring directly from the original container into the microwave vessel. Teflon® PFA microwave vessels rated to 120 psig (CEM, Matthews, NC) were used for the digestion according to the manufacturer's directions (13) and closed using the Capping Station (CEM, Matthews, NC). Various juices were selected for spiking. Samples and blanks were spiked at levels that were predicted for the diluted juice, and the spikes were digested concurrently with the juice samples to monitor any elemental losses in the digestion process. All products were prepared following the digestion procedure modified from the CEM application note for Fruit Juice and Pulp (14).

Digestion Procedure:
Step 1: Weigh ≤10 g **single-strength** juice into Teflon PFA digestion vessels.
Step 2: Add 10 mL concentrated, ultrapure HNO_3 and 2 mL concentrated, ultrapure H_2SO_4 to the sample.
Step 3: Cap the vessel in the capping station.
Step 4: Digest following the procedure in Table 3.
Step 5: Cool for approximately 5 minutes and vent vessels.
Step 6: Repeat Step 4 for juices containing pulp. Otherwise, proceed to Step 5.
Step 7: Cool for 5 minutes, vent, and open the vessels using the capping station.
Step 8: Add 3 ml ultrapure H_2O_2 to complete the digestion of remaining sugars
Step 9: When effervescence ceases, transfer the samples into clean containers and dilute to 100 mL with 18 megohm, distilled, deionized H_2O.
Step 10: Store the samples in clean high-density polyethylene bottles.
Step 11: Filter any residual pulp using acid-resistant syringe filters (Acrodisk product number 4497, Gelman Scientific, Ann Arbor, MI).

Table 3: Microwave Digestion Program for Juice Analysis

Parameter	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
Power (%)	10	20	0	15	0
Power (Watts)	51	141	0	96	0
Pressure (psig)	20	50	20	80	0
Run Time (min)	2	5	2	15	5
Time at Parameter (min)	2	5	2	15	5
Fan Speed (% of maximum)	100	100	100	100	100

ICP-OES Analysis
All analyses were performed on a Perkin-Elmer Optima 3000™ DV ICP-OES equipped with a dual-view torch, Scott-type spray chamber, and GemTip™ cross-flow nebulizer. A PerkinElmer AS-91 autosampler was used for sampling. Changing plasma views is accomplished using a computer controlled-mirror in the transfer optics. In one position (axial view), the optics are aligned to view down the axial channel of the plasma, in the other (radial view) radiation from the side of the plasma is reflected into the optics.

The Optima 3000 family of instruments features an echelle polychromator and a Segmented-array Charge-coupled Device (SCD) detector. This detector allows the simultaneous analyses of approximately 5000 analytical emission lines and provides the 2-4 best analytical lines for each element. The unique detector design permits simultaneous measurement of the analyte lines and spectral background that permits the best possible detection limits in either viewing configuration. This unique detector offers additional versatility

and freedom from spectral interferences over conventional direct reader-type simultaneous ICP-OES instruments. Because background and analyte measurements are performed simultaneously on this instrument, improved analytical sensitivity, analytical speed, and high sample throughput are advantages realized using Programmable Direct Reader technology instead of a sequential ICP-OES instrument. The plasma operating conditions are listed in Table 4 and the experimental detection limits, wavelength, and background correction points are listed in Tables 5-6. Differences in detection limits from those presented for the Optima 3000 in Table 2 may be attributed to the matrix. No attempt was made to optimize plasma conditions for any particular analyte or to optimize the procedure for the best sample throughput.

Table 4: Instrumental Conditions:

Parameter	Optima 3000 DV
RF Power:	1500 Watts
Nebulizer Flow:	0.75 L/min
Auxiliary Flow:	0.5 L/min
Plasma Flow:	15.0 L/min
Sample Flow:	1.5 mL/min
Plasma Height:	15 mm
Plasma Viewing:	Axial
Processing Mode:	Area
Auto Integration:	10 sec min – 50 sec max
Read Delay:	60 sec
Rinse Delay:	180 sec
Replicates:	3
Wavelengths:	Multiple
Background:	Manual selection of points

Table 5: Detection Limits, Wavelength Selection and Background Correction Points for Radial View

Element	Detection Limit mg/L	LOQ mg/L	Wavelength nm	Peak Window nm	Lower Bcg nm	Upper Bcg nm
Ca	1.5	5.0	317.935	0.0098	0.039	0.030
K	19	64	766.503	0.0233	0.140	0.139

Results

Values for each juice analyzed are presented in Tables 7-13 with available reference data (16-24). Little reference data was available for these materials. The Limit of Quantitation (LOQ) was defined as ten times the standard deviation of ten reads of the blank as a sample. This corresponds to 3.333 times the detection limit. Elements present at concentrations lower than the LOQ in the dilute solution are noted in the appropriate tables. Different dilution schemes would have permitted reporting of additional values. Table 14 shows good agreement for the major components determined using the radial and axial modes and indicates generally good agreement between different analytical wavelengths.

The ability to select viewing modes and analytical wavelengths depending upon desired sensitivity effectively extends the typical 5-6 order linear dynamic range quoted for ICP-OES even further. Tables 15-16 indicate that excellent spike recoveries were attained using both analytical modes.

Table 6: Detection Limits, Wavelength Selection and Background Correction Points for the Axial View

Element	Detection Limit mg/L	LOQ mg/L	Wavelength nm	Peak Window nm	Lower Bcg nm	Upper Bcg nm
Ag	0.5	1.6	328.070	0.0101	0.030	0.020
Al	160.	540.	308.213	0.0094	0.028	0.019
As	12.	38.	193.697	0.0059	0.017	0.030
B	65.	220.	182.528	0.0056	0.000	0.011
Ba	0.3	1.0	233.523	0.0072	0.021	0.029
Be	0.02	0.1	313.046	0.0096	0.039	0.029
Bi	16.	55.	222.819	0.0068	0.007	0.014
Ca	4.	13.	317.935	0.0098	0.039	0.030
Cd	0.2	0.7	214.434	0.0065	0.029	0.019
Co	0.8	2.7	228.619	0.0069	0.021	0.000
Cr	0.2	0.8	205.559	0.0063	0.012	0.025
Cu	1.1	3.6	324.759	0.0099	0.000	0.030
Fe	2.7	9.0	259.943	0.0079	0.023	0.016
Ga	2.0	7.	417.206	0.0127	0.025	0.064
In	8.	27.	230.602	0.0070	0.014	0.014
K404	2500.	8300.	404.717	0.0125	0.050	0.038
K766	6.7	22.	766.503	0.0233	0.140	0.139
Li	0.2	0.6	670.791	0.0204	0.081	0.102
Mg	4.	13.	279.082	0.0085	0.025	0.026
Mn	0.2	0.8	257.614	0.0078	0.024	0.023
Mo	1.5	5.	202.031	0.0062	0.013	0.018
Na	9.	30.	589.589	0.0182	0.055	0.073
Ni	0.6	1.9	231.604	0.0071	0.028	0.036
P213	1445.	480.	213.621	0.0065	0.039	0.020
P214	130.	440.	214.914	0.0065	0.000	0.020
Pb	3.5	11.	220.352	0.0067	0.013	0.000
Rb	12.	40.	780.021	0.0241	0.048	0.048
Se	4.5	14.	196.026	0.0061	0.018	0.019
Si	1.5	5.	212.413	0.0065	0.019	0.026
Sr	0.01	0.0	407.765	0.0125	0.025	0.038
Ti	0.2	0.7	337.277	0.0104	0.000	0.031
Tl	3.	10.	190.798	0.0058	0.012	0.017
U	9.	30.	367.012	0.0112	0.034	0.011
V	0.2	0.5	292.402	0.0090	0.027	0.018
Zn	0.5	1.7	213.858	0.0065	0.020	0.026

Table 7: Mean Results for Orange Juice in μg/mL Compared with Reference Values

Element	California Mean	RSD	FL Valencia Mean	RSD	Navel Orange Mean	RSD	Pineapple Orange Mean	RSD	Florida	McHard (16) Brazil	Mexican	Californian	Orange Juice (19)	(17)
Ag	< LOQ		< LOQ		< LOQ		< z		0.002-0.028	0.001 0.035	-0.010-0.132	<0.01		
Al	< LOQ		ND		ND		ND		0.041-0.155	0.062-5.67 0.736	0.206-0.364	0.098-		
As	ND		ND		ND		ND		< 0.015	< 0.015	NM	NM		
B	3.335	26.5	< LOQ		< LOQ		< LOQ		0.629-1.79	0.596-2.59	1.03-1.53	1.02-5.10		≤ 0.2
Ba	0.0771	0.5	0.0254	2.5	0.2117	0.9	0.0258	1.9	0.018-0.100	0.183-0.776	0.051-0.550	0.099-0.327		
Be	0.0028	114.7	ND		ND		ND		< 0.001	< 0.001	NM	NM		
Bi	ND		ND		ND		ND							50-240
Ca	123.3	0.4	61.30	1.6	103.0	0.5	85.78	0.9	67-123	77-120	87-135	102-150	60-120 £ 0.05	
Cd	ND		ND		ND		ND		< 0.01	< 0.01	NM	NM		
Co	< LOQ		< LOQ		< LOQ		< LOQ		< 0.01	< 0.01	< 0.01	< 0.01		
Cr	0.0176	124.1	0.0109	62.5	ND		< LOQ		0.003-0.021	0.002-0.064	0.004-0.011	0.009-0.031		≤ 5
Cu	0.5786	38.5	0.5345	1.8	0.3695	1.5	0.4351	1.2	0.239-0.460	0.154 0.400	-0.143-0.356	0.321-0.421		≤ 15
Fe	1.005	6.0	0.8792	1.5	1.016	15.0	0.5158	13.7	0.641-5.558	0.800-7.49	1.80-6.32	1.07-8.48		
Ga	ND		ND		ND		ND		0.016-0.042	0.022-.0147	.18-0.231	0.023-0.127		
In	< LOQ		ND		< LOQ		< LOQ		< 0.01	< 0.01	< 0.01	< 0.01	1100-2500	
K404	2205	1.5	2762	0.7	1754	1.3	2229	2.1	1520-2660	2030-3027	1245-2095	1741-2465	1400-2300	
K766	1875	0.4			1578	1.0	2054	1.5	1520-2660	2030-3027	1245-2095	1741-2465		70-170
Li	0.0142	9.3	< LOQ		< LOQ		< LOQ		0.002-0.008	0.002-0.007	0.003-0.005	0.003-0.026	70-150	
Mg	135.8	0.1	90.03	1.4	95.97	1.0	125.3	1.2	95-140	107-170	82-149	106-155		
Mn	0.2939	7.9	0.2428	0.9	0.1603	3.2	0.2692	4.1	0.173-0.316	0.218-0.794	0.207-0.466	0.278-0.921		
Mo	ND		ND		ND		ND		< 0.01	< 0.01	0.002-0.038	< 0.01		
Na	11.91	2.5	2.295	2.3	34.3	1.6	2.483	3.9	3-9	0.891-25.5	2.93-43.3	2.51-9.78	114-196 ≤0.3	
Ni	ND		0.0755	3.9	ND		ND		0.008-0.067	0.007-0.092	0.009-0.223	0.016-0.062		
P213	220	0.7	175.3	0.9	158.4	1.0	152.8	0.9	124-240	155-308	104-303	193-309		
P214	220.4	0.9	176.3	0.9	158.6	1.2	153	1.4	124-240	155-308	104-303	193-309		
Pb	ND		0.1674	4.1	ND		ND		< 0.01	< 0.01	NM	NM		
Rb	1.248	2.8	1.026	2.4	1.381	1.4	1.002	0.3	0.236-0.741	2.64-6.72	0.630-3.403	0.757-3.73		
Se	0.3363	13.4	0.3377	10.8	0.302	29.6	0.3734	13.5						≤5
Si	3.249	7.6	0.7186	5.6	1.456	3.8	0.5894	1.1						
Sr	0.5368	0.2	0.0933	1.2	0.5209	0.4	0.1612	1.1	0.095-0.979	0.288-1.09	0.325-0.713	0.395-0.733		
Ti	< LOQ		ND		< LOQ		< LOQ		0.002-0.022	0.004-0.357	0.005-0.020	0.012-0.025		
Tl	ND		ND		ND		ND							
U	ND		ND		ND		ND							
V	< LOQ		ND		< LOQ		ND		ND	ND	ND	0.001-0.10		
Zn	0.357	18.5	0.3201	4.6	0.3401	80.0	0.3098	15.0	0.242-0.480	0.255-0.527	0.267-0.449	0.249-0.538		

ND: Below detection limit; LOQ: Limit of Quantitation

Table 8: Mean Results for Other Citrus Fruit in µg/mL Compared with Reference Values

Element	Ruby Red Grapefruit Mean	RSD	Lime Mean	RSD	Tangerine Mean	RSD	Grapefruit Juice (17)	(18)	Lime Juice (15, 23)	Tangerine Juice (15)
Ag	ND		ND		ND					
Al	<LOQ		ND		<LOQ					
As	ND		ND		ND		≤0.2			
B	ND		10.45	99.8	2.779	30.1				
Ba	<LOQ		0.0638	190.0	0.0349	4.5				
Be	0.0013	7.7	ND		0.0008	9.5				
Bi	<LOQ		<LOQ		ND					
Ca	64.47	1.2	50.25	174.3	69.69	0.1	50-160	> 50	90-220	180
Cd	ND		ND		ND		≤0.05			
Co	<LOQ		ND		< LOQ					
Cr	ND		0.0182	212.0	ND					
Cu	0.4939	2.2	<LOQ		0.5926	2.1	≤ 5		0.30	0.25
Fe	0.3866	9.7	0.8732	210.2	0.948	18.6	≤ 15		0.30-3.0	2.0
Ga	ND		<LOQ		ND					
In	<LOQ		<LOQ		<LOQ					
K404	1221	0.6	251.1	154.5	1984	3.8	1000-2500	> 1000	1090-1500	1780
K	1261	0.6	278.6	174.0	1942	1.3	1000-2500	> 1000	1090-1500	1780
Li	<LOQ		0.0066	204.0	<LOQ					
Mg	79.45	0.2	23.24	174.2	129.4	1.6	70-170	>85	60-110	80
Mn	0.1141	1.3	0.0665	194.1	0.6043	4.6			0.08	0.37
Mo	ND		ND		ND					
Na	5.867	2.2	78.23	173.2	7.473	6.9	≤30	<50	10-30	10
Ni	ND		<LOQ		0.1241	126.0				
P213	146	0.4	16.00	243.3	110.5	3.3			70	140
P214	153.6	0.3	16.17	250.3	111.9	3.7			70	140
Pb	ND		<LOQ		ND		≤0.3			
Rb	<LOQ		<LOQ		<LOQ					
Se	0.2555	5.6	<LOQ		0.3677	9.3				
Si	0.2502	25.9	5.224	158.6	0.7349	3.7				
Sr	2.577	1.1	0.3464	173.9	0.0828	2.8				
Ti	0.0083	20.0	0.0828	150.3	<LOQ					
Tl	ND		ND		ND					
U	ND		<LOQ		ND					
V	<LOQ		0.2444	173.3	ND					
Zn	0.8934	48.0	0.0584	537.9	0.2669	31.2	≤ 5		0.6-1	0.30

ND: Below detection limit LOQ: Limit of Quantitation

Table 9: Mean Results for Stone Fruit (*Prunus* spp) Cultivars in μg/mL Compared with Reference Values

Element	Apricot Mean	RSD	Sour Cherry Mean	RSD	Peach Mean	RSD	Plum Mean	RSD	Prune Mean	RSD	Apricot Nectar (15)	Cherry (15)	Peach Nectar (15)	Plum Raw (15, 20)	Prune (15)
Ag	< LOQ		< LOQ		< LOQ		ND		< LOQ						
Al	ND		73.07	3.3	ND		< LOQ		20.45	3.7					
As	ND		ND		ND		ND		ND						
B	< LOQ		ND		2.216	12.2	2.394	74.0	6.839	16.7					
Ba	0.0215	5.1	0.0169	0.5	0.0281	2.9	0.0741	3.6	0.413	1.1					
Be	< LOQ		0.0015	4.1	ND		0.0016	11.1	0.0036	50.4					
Bi	ND		< LOQ		ND		ND		ND						
Ca	24.73	0.4	64.2	0.5	21.63	1.7	26.67	0.6	109.9	0.9	70	160	50	40-80	120
Cd	ND		< LOQ		ND		ND		ND						
Co	< LOQ		ND		< LOQ		< LOQ		< LOQ						
Cr	0.0134	27.1	ND		ND		ND		0.015	48.8					
Cu	0.1851	14.8	0.2235	0.4	0.6003	2.8	0.3648	2.0	0.319	29.8	0.73	1.04	0.69	0.43	0.68
Fe	0.5111	1.8	1.742	0.2	< LOQ		0.1639	51.8	6.255	0.8	3.8	3.2	1.9	1-4	11.80
Ga	ND		ND		ND		ND		ND						
In	ND		< LOQ		ND		< LOQ		ND						
K404	546.7	4.1	1012	1.1	2185	1.2	616.5	2.7	2029	2.3	1140	1730	400	1200-1900	2760
K	590.7	3.5	1021	0.2	2054	0.8	703.1	1.0	2066	1.0	1140	1730	400	1200-1900	2760
Li	ND		ND		< LOQ		< LOQ		0.0228	3.9					
Mg	32.98	3.9	63.81	0.2	62.83	2.1	30.39	0.6	104.2	1.2	50	90	40	40-70	140
Mn	0.2725	1.1	0.352	0.3	0.4581	1.4	0.1769	2.0	1.883	1.0					
Mo	ND		ND		ND		ND		ND						
Na	62.21	13.6	1.644	1.7	1.88	2.4	23.92	4.0	54.64	4.3	30	30	70	0-30	40
Ni	0.0242	19.4	ND		0.0231	24.6	ND		0.0338	24.3					
P213	45.77	5.6	121.5	0.2	165.2	0.8	49.54	3.3	184.4	0.9	90	150	60	100	250
P214	42.74	2.4	113.0	0.3	166.8	0.5	49.59	4.2	190.4	1.0	90	150	60	100	250
Pb	ND		ND		ND		ND		ND						
Rb	0.6265	45.7	0.135	5.2	3.014	1.2	< LOQ		1.864	4.8					
Se	0.2191	7.9	0.2309	7.7	0.2707	5.2	0.3799	10.6	0.3695	9.0					
Si	3.707	1.3	1.335	1.8	0.0909	82.3	3.7	1.6	32.57	3.5					
Sr	0.1566	5.8	0.0338	0.1	0.0128	4.1	0.1052	1.2	0.8805	1.0					
Ti	< LOQ		< LOQ		ND		< LOQ		0.1101	0.4					
Tl	ND		ND		ND		ND		< LOQ						
U		ND		ND		ND		ND		ND					
V	< LOQ		< LOQ		ND		ND		< LOQ						
Zn	0.3300	5.6	0.1101	17.6	0.7957	2.5	0.1067	20.7	1.132	2.4	0.9	1.0	0.8	1.0	2.1

ND: Below detection limit; LOQ: Limit of Quantitation

Table 10: Mean Results for Grape Cultivars in μg/mL Compared with Reference Values

Element	Concord Grape Mean	RSD	Red Grape Mean	RSD	White Grape Mean	RSD	Grape (15)
Ag	< LOQ		< LOQ		< LOQ		
Al	< LOQ		6.042	9.9	7.936	5.5	
As	ND		ND		ND		
B	2.803	80.4	< LOQ		< LOQ		
Ba	0.4086	1.1	0.027	2.4	0.2318	0.5	
Be	< LOQ		0.0017	9.4	0.007	2.3	
Bi	ND		ND		< LOQ		
Ca	100.8	1.0	42.43	0.8	182.4	0.3	90
Cd	< LOQ		ND		ND		
Co	< LOQ		< LOQ		< LOQ		
Cr	0.2677	1.5	ND		0.0452	2.5	
Cu	0.4083	0.5	1.878	0.4	0.3811	2.2	0.28
Fe	1.77	2.3	ND		5.217	0.1	2.4
Ga	ND		ND		ND		
In	ND		ND		< LOQ		
K404	507.2	4.3	883.2	2.8	236.2	1.9	
K766	550.5	1.4	924.8	2.3	289.4	0.9	1320
Li	< LOQ		ND		0.0066	4.3	
Mg	113	1.0	63.88	2.5	128.7	0.7	100
Mn	4.893	0.6	0.4055	0.9	3.617	0.4	3.6
Mo	< LOQ		ND		0.2162	0.5	
Na	20.47	3.7	3.613	3.4	42.1	1.2	30
Ni	< LOQ		ND		< LOQ		
P213	93	2.7	189.1	1.8	110.6	0.5	
P214	90.56	3.6	194.8	1.6	114.8	0.5	110
Pb	< LOQ		ND		< LOQ		
Rb	0.6865	0.6	< LOQ		< LOQ		
Se	0.2708	26.3	0.3016	45.9	0.3768	3.4	
Si	9.805	2.2	5.538	2.1	12.20	0.6	
Sr	0.3661	1.1	0.1086	0.6	0.6318	0.3	
Ti	0.1053	5.0	< LOQ		0.1681	1.5	
Tl	ND		ND		ND		
U	ND		ND		ND		
V	0.3437	1.0	< LOQ		0.8553	0.4	
Zn	0.8165	54.0	0.609	51.7	0.8318	19.4	0.5

ND: Below detection limit LOQ: Limit of Quantitation

Table 11: Mean Results for Berries in µg/mL Compared with Reference Values

Element	Blackberry Mean	RSD	Blueberry Mean	RSD	Boysenberry Mean	RSD	Raspberry Mean	RSD	Strawberry Mean	RSD	Blackberry Raw (15)	Blueberry Raw (15)	Boysenberry Frozen (15)	Raspberry Juice (19)	Strawberry Raw (15)
Ag	< LOQ		< LOQ		< LOQ		< LOQ		ND						
Al	70.70	13.0	91.88	2.0	89.25	3.0	7.983	9.7	< LOQ						
As	ND		ND		ND		ND		ND						
B	ND		ND		ND		2.773	77.2	2.812	11.5					
Ba	0.6458	1.0	0.1665	5.3	0.7793	0.1	1.212	2.3	0.0746	1.4					
Be	0.0015	14.2	0.0017	0.7	0.0015	4.0	0.0009	9.8	0.001	33.0					
Bi	< LOQ		< LOQ		< LOQ		ND		ND						
Ca	78.77	0.3	31.25	3.1	131.7	0.1	251.2	2.1	43.89	0.8	320	60	270	110-230	140
Cd	< LOQ		< LOQ		< LOQ		ND		ND						
Co	< LOQ		ND		< LOQ		< LOQ		< LOQ						
Cr	0.0085	5.8	ND		< LOQ		ND		0.0199	210.3					
Cu	0.5646	1.9	0.1669	5.6	0.3592	2.3	0.7182	1.7	0.1752	10.8	1.40	0.61	0.80		0.49
Fe	28.74	0.7	ND		2.391	1.2	4.979	1.4	ND		5.7	1.7	8.5		3.80
Ga	ND		ND		ND		ND		< LOQ						
In	< LOQ		< LOQ		< LOQ		ND		< LOQ						
K404	941.8	0.6	238.4	0.4	2010	0.4	1381	2.0	500.9	1.3	1960	890	1390	1300-2800	1660
K766	980.7	0.3	250.1	1.0	1838	1.0	1485	1.5	571.5	0.4	1960	890	1390	1300-2800	1660
Li	ND		ND		ND		< LOQ		< LOQ						
Mg	90.84	1.0	23.15	0.8	181	0.5	190	1.5	46.26	1.1	200	50	160	110-230	100
Mn	9.602	0.7	4.515	2.6	6.81	0.3	3.037	0.9	0.8858	4.1	12.91	2.82	5.47		
Mo	ND		ND		ND		ND		ND						
Na	31.48	2.1	3.814	0.2	2.269	0.9	1.045	24.8	3.968	3.4	0	60	10	40 max	10
Ni	0.0206	32.6	ND		0.0724	2.0	0.0816	58.4	< LOQ						
P213	59.52	2.5	18.89	5.0	138.7	0.3	204.0	2.5	50.4	3.8	210	100	270	98-244	190
P214	54.02	2.6	15.37	6.1	129.0	0.5	209.9	2.5	49.57	4.0	210	100	270	98-244	190
Pb	< LOQ		ND		< LOQ		ND		ND						
Rb	0.8111	0.8	0.7573	1.4	1.394	2.1	3.08	2.2	< LOQ						
Se	0.2046	9.4	0.0846	10.3	0.2452	12.4	0.2639	45.1	< LOQ						
Si	0.5593	10.4	0.9454	13.7	2.253	4.2	1.681	16.0	2.13	1.3					
Sr	0.2619	0.9	0.0406	3.9	0.9523	0.5	2.232	1.9	0.3001	1.1					
Ti	< LOQ		< LOQ		0.1007	2.6	0.095	10.0	< LOQ						
Tl	ND		ND		ND		ND		< LOQ						
U	< LOQ		ND		ND		ND		ND						
V	< LOQ		< LOQ		< LOQ		< LOQ		ND						
Zn	3.587	0.3	0.0671	10.4	1.898	0.2	2.297	10.1	0.046	75.0	2.7	1.1	2.2		1.3

ND: Below detection limit; LOQ: Limit of Quantitation

Table 12: Mean Results for Tropical Fruit in μg/mL Compared with Reference Values

Element	Banana Mean	Banana RSD	Kiwi Mean	Kiwi RSD	Mango Mean	Mango RSD	Pineapple Mean	Pineapple RSD	Banana Raw (21, 22)	Kiwi Raw (15)	Mango Raw (15, 21)	Pineapple Raw (21, 24)
Ag	ND		< LOQ		0.0221	179.7	< LOQ		0.01			
Al	80.25	8.5	9.025	6.9	< LOQ		< LOQ		0.45			
As	ND		ND		ND		ND		0.019			
B	ND		< LOQ		< LOQ		< LOQ					
Ba	0.1476	1.6	1.12	1.3	0.291	2.3	0.0127	5.5	0.140			
Be	0.0015	17.7	0.003	5.1	0.0045	179.8	< LOQ					
Bi	< LOQ		< LOQ		ND		ND		0.007			
Ca	17.43	1.2	235.9	1.1	63.31	2.1	41.17	2.0	64.4	260	100	172
Cd	< LOQ		ND		< LOQ		ND		0.014			
Co	ND		< LOQ		< LOQ		< LOQ		0.007			
Cr	ND		< LOQ		0.0696	148.1	ND		0.122			
Cu	0.3937	4.1	0.6622	2.0	1.294	58.3	0.4648	14.7	2.1-5.4		1.10-8.6	1.2-8.9
Fe	0.6743	17.4	6.871	1.3	1.16	21.9	0.2625	20.4	6.7-33	4.1	1.3-77.6	1.3-102
Ga	ND		ND		ND		ND		0.003			
In	< LOQ		< LOQ		< LOQ		< LOQ					
K404	1075	0.4	2800	2.7	1617	2.3	477.1	6.0		3320	1560	1440
K766	1090	1.0			1407	4.0	537.9	4.3	3589	3320	1560	1440
Li	ND		0.0278	8.4	< LOQ		ND		0.003			
Mg	97.76	1.1	105.4	0.9	87.89	2.2	47.71	0.7	327.8	300	90	184
Mn	0.7989	2.6	1.441	1.0	0.7915	8.7	5.541	3.1	3.43-5.7		0.27-25	8.8-135
Mo	ND		ND		ND		ND		0.079			
Na	0.514	90.2	39.96	2.7	3.444	3.0	0.6195	20.5	29.8	50	20	16.2
Ni	ND		ND		< LOQ		ND		0.064			
P213	80.34	0.4	114.9	1.0	96.81	2.4	14.63	13.9	312	400	110	49.8
P214	72.67	0.2	121.1	1.5	93.08	3.2	13.45	17.8	312	400	110	49.8
Pb	< LOQ		< LOQ		ND		ND		0.024			
Rb	< LOQ		4.943	2.8	3.479	4.4	0.4459	49.2	.24			
Se	0.1761	14.4	0.3001	6.2	0.3947	2.3	0.2876	9.5	0.009			
Si	3.878	28.4	12.12	1.3	2.381	16.6	11.98	0.9	76.4			
Sr	0.1297	0.2	1.744	0.8	0.5121	2.9	0.0604	4.4	0.360			
Ti	0.0439	157.6	0.1007	3.3	< LOQ		< LOQ		0.055			
Tl	ND		ND		ND		ND					
U	ND		ND		ND		ND					
V	< LOQ		0.0408	0.6	< LOQ		ND		0.003			
Zn	0.6880	54.5	0.9411	6.9	0.8476	31.8	0.0609	34.1	2.8-7.8		0.40-3.2	1.2-10.1

ND: Below detection limit; LOQ: Limit of Quantitation

Table 13: Mean Results for Other Fruit in μg/mL Compared with Reference Values

Element	Red Currant Mean	RSD	Pear Mean	Pear RSD	Red/White Currants Raw (15)	Pear Nectar (15)
Ag	< LOQ		< LOQ			
Al	122.5	4.2	ND			
As	ND		ND			
B	< LOQ		< LOQ			
Ba	0.7174	1.0	0.6488	0.5		
Be	0.0011	8.2	0.0373	170.0		
Bi	< LOQ		ND			
Ca	200.5	0.6	65.73	0.8	330	50
Cd	0.0112	2.7	ND			
Co	< LOQ		< LOQ			
Cr	< LOQ		ND			
Cu	0.3721	0.6	2.79	117.2	1.07	0.69
Fe	8.550	1.3	0.7001	7.5	10.00	1.9
Ga	ND		ND			
In	< LOQ		ND			
K404	2783	1.6	978.9	2.5	2750	2400
K766			1100	1.1	2750	400
Li	ND		< LOQ			
Mg	94.61	0.6	76.81	0.2	130	40
Mn	1.152	0.9	0.3695	4.8	1.86	0.19
Mo	ND		ND			
Na	19.34	3.8	2.309	8.0	10	70
Ni	0.1209	4.3	< LOQ			
P213	283.2	0.6	86.21	5.5	440	60
P214	266.6	0.5	82.77	6.1	440	60
Pb	< LOQ		ND			
Rb	0.9864	3.7	1.375	5.7		
Se	0.3212	10.3	< LOQ			
Si	5.553	6.0	0.7727	17.0		
Sr	1.251	0.7	0.5912	1.2		
Ti	0.4314	0.4	< LOQ			
Tl	ND		< LOQ			
U	< LOQ		ND			
V	0.0223	1.9	ND			
Zn	1.480	42.4	0.6203	13.9	2.3	0.8

ND: Below detection limit; LOQ: Limit of Quantitation

Table 14: Comparison of Mean Results by Viewing Modes for Selected Fruit in µg/mL Compared with Reference Values

Viewing Mode	Element	Banana Mean	RSD	Blackberry Mean	RSD	Blueberry Mean	RSD	Boysenberry Mean	RSD	Sour Cherry Mean	RSD	Red Currant Mean	RSD
Radial	Ca	17.64	2.4	75.58	1.0	30.4	1.2	132.9	2.3	62.72	0.4	200.3	0.6
	K766	1208	0.9	1037	0.4	285	0.2	2074	3.0	1115	0.3	2729	1.4
Axial	Ca	17.43	1.2	78.77	0.3	31.3	3.1	131.7	0.1	64.2	0.5	200.5	0.6
	K404	1075	0.4	941.8	0.6	238	0.4	2010	0.4	1012	1.1	2783	1.6
	K766	1090	1.0	980.7	0.3	250	1.0	1838	1.0	1021	0.2	NM	NM

NM: Not Measured

Table 15: Spike Recoveries for Blanks and Juices Axial Viewing Mode

Element	Blank (%)	Blank (%)	Blank (%)	Apricot (%)	Concord Grape (%)
Ag	92.8	94.1	108.3	109.3	97.8
Ba	101.5	99.9	104.8	93.8	96.5
Be	99.1	100.4	105.5	101.6	101.3
Bi	100.8	100.4	107.4	107.4	97.4
Ca	98.7	100.5	103.0	100.1	98.5
Cd	102.1	100.0	104.9	93.0	97.5
Co	99.7	100.3	104.5	104.6	94.8
Cr	101.2	99.9	104.4	94.7	97.9
Cu	98.8	99.4	106.2	102.5	97.6
Fe	96.5	97.8	103.1	100.9	92.9
Ga	100.5	99.2	107.2	93.9	93.6
In	103.8	99.1	105.8	100.7	95.4
K404	95.2	100.2	104.6	99.5	91.4
K766	99.0	99.6	104.2	91.1	91.6
Li	98.7	99.1	104.4	101.8	96.9
Mg	98.4	100.3	104.8	104.3	97.7
Mn	97.6	99.1	104.4	101.9	80.9
P213	97.1	96.8	100.6	114.1	105.8
P214	97.5	95.8	100.1	107.5	109.3
Pb	100.9	99.2	103.9	92.9	95.8
Se	104.0	98.4	107.6	110.8	111.8
Sr	103.1	100.5	104.7	94.0	92.5
Tl	99.8	100.4	104.7	91.1	84.0
U	97.6	98.8	107.7	98.5	91.9
V	98.7	99.5	105.1	101.0	95.9
Zn	101.0	100.0	105.4	98.3	102.2

Table 16: Spike Recoveries for Blanks and Juices Radial Viewing Mode

Element	Blank (%)	Blank (%)	Blank (%)	Apricot (%)	Concord Grape (%)
Ca	98.3	98.3	103.3	101.3	106.2
K766	98.9	98.9	101.9	100.2	107.7

Conclusion

This work demonstrates that ICP-OES is applicable to the determination of trace elements in fruit, juice and juice products. Axially viewed plasmas are amenable to trace level work and give detection limits comparable to GFAAS and permit the determination of nutrients not previously possible by ICP-OES. All minerals stipulated by NLEA may be determined in juice using ICP-OES, and it is evident that the technique is an effective tool for the analyst attempting to meet the challenges imposed by NLEA. Trace elements important in establishing geographical origin can be determined simultaneously with NLEA elements, and other elements of interest may be selected as needed. Good agreement with available reference values was achieved. Excellent spike recoveries were attained for all juice matrices. Sample preparation time, which was the primary limitation to sample throughput, was minimized due to the wide linear dynamic range and useful analytical range of the dual-view ICP-OES. All nutrients were determined simultaneously in all samples without multiple dilution/analysis steps. Levels attainable were comparable with GFAAS. Although no attempts were made to optimize sample throughput, actual instrumental sample throughput was impressive relative to current validated methods and to GFAAS. Microwave digestion was shown to be a useful sample preparation procedure allowing acceptable precision, spike recoveries, and good agreement with available reference values and with classical digestion methodology. The dual-view capabilities of the instrument effectively extend the useful analytical range of ICP-OES.

References

[1]   Miller-Ilhi, N. Appl. Spectrosc. 47, 14A (1993).

[2]   Federal Register, 58, 632-690, 2066-2964, January 6, 1993.

[3]   Instrument and Business Outlook, 12 (2/1993)

[4]   Official Methods of Analysis of the Association of Official Analytical Chemists, Fifteenth Edition, 1990,

[5]   The Referee, 17, 9 (9/1993)

[6]   The Referee, 17, 7, (7/1993).

[7]   Federal Register, 58, 61, 17233, (April 1, 1993).

[8]   Florida Statutes, Sections 500.10 (2) (A) and 500.10 (B) (1978).

[9]   Adulteration of Fruit Juice Beverages, ed. S. Nagy, J.A. Attaway, M.E. Rhodes, Marcel Dekker, Inc. (1988).

[10]   Schwartz, R.S. and Hecking Le T., JAAS. 6, 637, 1991.

[11]   Paul Krampitz and Karen W. Barnes, Trace Metals Determination in High Purity Vegetable Oil Using PerkinElmer Optima 3000XL ICP System, Presented at the 108th AOAC International Annual Meeting and Exposition, Portland, OR, 9/14/94.

[12]   The Guide to Techniques and Applications of Atomic Spectroscopy, PerkinElmer Instruments, Norwalk, CT, 1993, 5.

[13]   CEM MDS 2100 Operation Manual, Revision 12-92, 27-36.

[14]   CEM Application Note PM-3 (1988) Revision 6-88.

[15]   United States Department of Agriculture Human Nutrition Information Service Handbook Number 8-9 (revised 1982), US Government Printing Office, Washington D.C., pp 37, 38, 60, 90, 34, 139, 184, 269.

[16]   McHard, J.A., Foulk, S.J., Jorgensen, J.L., Bauer, S., & Winefordner, JD. (1980) in Citrus Nutrition and Quality, ACS Symposium Series, Vol. 143, S. Nagy, and J.A. Attaway (Eds.), American Chemical Society, Washington D.C., pp. 382-383.

[17]   Afnor-Unpjf Fruit Juice Specifications, 1988.

[18]   Analytical Reports, Dr. Allan Brause, Analytical Chemical Services of Columbia, Inc. 1993.

[19]   RSK Values The Complete Manual, 1987 edition.

[20]   Wills, R.B.H, Scriven, F.M., and Greenfield, H., J. Sci. Food Agric, 34, 1383, 1983.

[21]   Benzo, Z., Schorin, H., and Velosa, M., J. Food Sci., 51, 222, 1986.

[22]   Cowgill, U.M., Biological Trace Element Research, 3, 33, 1981.

[23]   Wills, R.B.H., Lim J.S.K., Greenfield, H., Food Technology in Australia, 37, 7, 308, 1985.

[24]   Sims, R.L., Mullen, L.M., Milne, D.B., Journal of Food Composition and Analysis, 3, 327, 1990.

Acknowledgment

PerkinElmer™
instruments.

Visit our website at **www.perkinelmer.com**

PerkinElmer, Optima 3000, and GemTip are trademarks of PerkinElmer, Inc.
Teflon is a registered trademark of E.I. duPont deNemous & Co., Inc.

D-6259
ICPAS79

© 1992 - 1999 PerkinElmer, Inc.   Printed in U.S.A. ⊕

KG129901