Comparison Study of Four Atomic Spectrometric Methods for the Determination of Metallic Constituents in Orange Juice

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Metal constituents in orange juice have been determined by four atomic spectral methods—flame atomic absorption spectrometry, flame atomic emission/fluorescence spectrometry, dc plasma atomic emission spectrometry, and inductively coupled plasma atomic emission spectrometry. Substantial differences between methods were observed with regard to speed, convenience, precision, detection limits, and interpretation of analytical calibration curves near the detection limits. In general, however, all atomic spectral methods used in the comparison gave plausible agreement in the values obtained.

Some of the present authors (1) have previously published a study on the use of flame atomic absorption spectrometry (FAAS) to determine several elements in orange juice. Since the time of that publication, direct current plasma atomic emission spectroscopy (DCPAES) and inductively coupled atomic emission spectroscopy (ICPAES) have become increasingly popular as sources for atomic emission spectrometry (2–8), and interest is growing in flame atomic fluorescence spectrometry (FAFS) as better instrumentation becomes available (9–12). It seemed of timely interest to compare the measurement of trace metals in a practical analytical problem such as the analysis of orange juice using these atomic spectral methods and to compare the results with already published values obtained by flame atomic absorption spectrometry (FAAS). In this paper, the authors compare values obtained by DCPAES, ICPAES, and FAFS with those from FAAS. Also in this paper, comparative analytical figures of merit using two sets of replicate samples dissolved on the one hand in dilute hydrochloric acid and on the other in dilute nitric acid are given.

EXPERIMENTAL

Apparatus. The ICPAES and FAFS systems used in this study have already been described (13, 14). It should be noted that the signal of the FAFS system (wavelength modulated) consisted of the sum of atomic fluorescence and atomic emission. The DCPAES (Spectraspan II) system also has been described by the commercial supplier, Spectrametrics, Inc., and by others who have used the equipment. The Spectraspan II was modified in this study by the replacement of the Spectrajet II plasma (15, 16) source with the recently designed Spectrajet III. The instrumental parameters and source conditions are listed in Table I. In Table II are listed the wavelengths used for the various elements.

Reagents. Analytical grade reagents were used in preparing all standard solutions. Copper, iron, magnesium, manganese, and zinc metals were dissolved in acid and diluted to volume. Barium, calcium, potassium, rubidium, and sodium standard solutions were prepared from the dry carbonates. To provide a sample-matching environment for the trace elements—barium, copper, iron, manganese, rubidium, and zinc—a solution was prepared con-

taining calcium, magnesium, potassium, and phosphorus (as phosphate) in the ratios that exist in frozen concentrated orange juice (FCOJ). Mixtures containing suitable concentration ranges for the preparation of analytical calibration curves for the measurement of the trace elements were prepared by dilution of stock 1000-ppm aqueous analyte standard solutions in suitable volumes of the matrix. The standards used for the preparation of analytical curves for the determination of calcium, magnesium, potassium, and sodium were prepared by dilution of the appropriate stock solutions with the required dilute acid. These principal elements taken together provided the only matrix for the preparation of their respective analytical curves. No additional matrix was used for these latter elements because of the extreme dilution (400 to 1 based on starting weight of FCOJ) used in the final measurement. In actuality, phosphorus is the only significant element present in the *trace* analyte matrix which is absent from the analysis mixture for the *principal* elements.

Sample Preparation. Two sets of seven replicate 10-g samples of a commercial brand of Florida FCOJ were weighed into 100-mL platinum dishes. The 14 separate samples were dried and partially decomposed to carbonaceous residues under heat lamps. Final ashing was completed by ignition in a muffle furnace. The ignition was initiated slowly starting with a cold furnace and increasing the temperature to 550 °C over a period of 4 h. Ashing was continued at 550 °C for a period of 16 h, a length of time which was sufficient to produce a white carbon-free residue. One set of ashings was dissolved in 50 mL of 0.1 M hydrochloric acid and the other set was dissolved in 50 mL of 0.1 M nitric acid. Further dilution was made in water to bring the analyte elements and natural sample matrix to predetermined concentration levels for analysis.

RESULTS AND DISCUSSION

Measurement Methods. The three types of instrumentation used in this study (ICPAES, DCPAES, and FAFS) have already been described in the section on apparatus. A further note with regard to the FAFS system is that it is computer controlled and can be considered to be a sequential multielement device. However, it was used in the single element mode in an effort to make it more comparable with the other atomic spectral methods used in this study, all of which were single-element devices.

There are some differences in methodology, aside from instrumentation, between this study and that reported previously using FAAS (1). These differences are principally as follows.

First, because the eight different brands of Florida juice analyzed in the FAAS study were found to be remarkably uniform in metals content and to simplify comparison, only one of these brands was selected for evaluation in the present study. There was a time lapse, of course, between samplings for the two studies and it follows that the sample in the current study would not necessarily be identical to the same brand sample in the FAAS study. For the reader's interest and benefit in making comparisons, brand number seven of the FAAS study was used in this study.

Second, the samples in the present study were prepared for analysis by dry ashing instead of by acid hydrolysis. When acid hydrolysis is used for sample preparation as was the case for the FAAS study, there is a considerable amount of a sugar-like degradation product left in the analyte solution and

Table I. Instrument Description and Parameters

	ICPAES[a]	DCPAES[b]	FAFS[c]	
source gas	argon	argon	air/acet	N₂O/acet
gas flows	cooling gas, 16 L/min neb. gas, 0.5 L/min 30 psi	neb. gas, 20 psi plasma, 80 psi sleeves, 50 psi	air, 8.2 L/min aux air, 0.5 L/min acet, 2.3 L/min sheath, 9 L/min	N₂O, 7.5 L/min aux N₂O, 2 L/min acet, 2.3 L/min sheath, 12 L/min
sample uptake rate	1.5 mL/min	1.2 mL/min	5 mL/min	5 mL/min
spectral band pass	0.04 nm	0.006 nm	0.4 nm	0.4 nm
PM tube	Hamamatsu R818 185-880 nm	Hamamatsu R777 185-930 nm	RCA 1P28 210-650 nm	RCA 1P28 210-650 nm

[a] For a complete description of the source, spectrometer, and operating characteristics see ref. 13. [b] The source was Spectrajet III (Spectrameterics Inc, Andover, Mass.). [c] See ref. 14.

Table II. Spectral Lines Used for Analysis

element	ICPAES, nm	DCPAES, nm	FAFS, nm	FAAS,[a] nm
Ba	455.40	455.40	553.55	b
Ca	393.37	422.67	422.67	422.67
Cu	b	324.75	324.75	324.75
Fe	371.99	358.12	371.99	248.33
K	766.49	769.9	404.41	404.41
Mg	279.55	285.21	285.21	285.21
Mn	403.08	403.08	279.48	279.48
Na	588.99	589.59	589.59	589.59
Rb	780.02	780.02	b	b
Zn	b	213.86	213.86	213.86

[a] See ref. 1. [b] Values not measured, see text.

this, added to the inorganic solids, always contributes sample introduction problems in many types of atomic spectral introduction systems.

Before discussing the third point of departure, it is necessary to clarify what the authors mean by *trace* elements. It was stated in the section under Reagents that a synthetic matrix was used for the elements—barium, copper, iron, manganese, rubidium, and zinc. Most of these elements were at concentrations in the sample under study of less than 1 ppm and, therefore, they were analyzed at similar (comparatively low) dilution ratios. As a result, this group of elements were arbitrarily classified as *trace*. The elements—calcium, magnesium, and potassium—were found to be at substantially higher concentrations and sodium at a moderately higher concentration. Therefore, this latter group is termed *principal* elements and they were analyzed for in much more dilute solution. This higher dilution ratio abated much of the interelement influence on analyte signal. It was found, for example, that at the dilutions used (400 to 1 based on the original sample weight), there was no influence of phosphate on the calcium signal at or near the expected concentration ratios in the sample.

Finally then, the standards used in the study reported on here were constituted in a different manner from the previous FAAS study. They were not processed through the sample preparation step and, as pointed out above, the standards for the *trace* elements groups were made by matching matrices in the reference solutions as closely as possible to that expected from ashed orange juice. Although this action is somewhat similar to that taken in the FAAS study, in the present instance the trace element content of the standards was varied in a matrix of *constant composition* rather than adhering to a *fixed ratio* of all elements as was done in the FAAS study. It was found that this was important because of certain interelement effects. In orange juice the trace element content varies in a matrix containing a potassium content which is high and relatively constant in samples from widely different origins. Potassium enhances the barium signal especially when
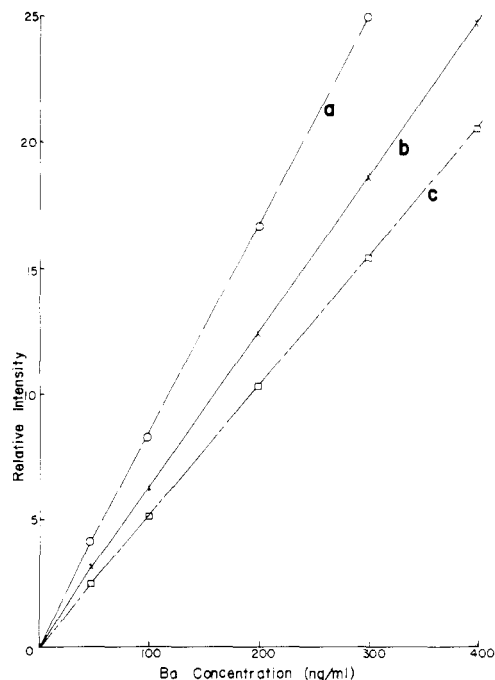

Figure 1. Effect of potassium on barium calibration curves using DCPAES. (a) Analytical curve for barium in matrix containing constant K concentration (800 ppm) in 0.1 M HNO₃. (b) Analytical curve for barium in matrix containing constant K/Ba ratio (4000/L) in 0.1 M HNO₃. (c) Analytical curve for barium in 0.1 M HNO₃

using the DCPAES instrumentation. It was found that this enhancement depends not entirely on the ratio of potassium to barium but also on the total concentration of potassium present in the matrix (see Figure 1). The enhancement effect of potassium on barium using the DCPAES was observed using either the atom line (553.55 nm) or the ion line (455.40 nm) as illustrated in Figure 2. This anomalous behavior has also been observed and reported on elsewhere (17). In addition, the ICPAES showed marked enhancement of barium by potassium at the atom line but some very slight depression at the ion line.

Comparison of Analytical Results. The results of the analytical work using the various instrument types are presented in Table III. These results are given in summary form for each element according to the type of acid used for effecting solution of the ash and according to the type of instrumentation used. Also presented for comparison is a recapitulation of the atomic absorption values referred to previously. There are differences between the nitric and hydrochloric acid sets, but the differences do not seem to be particularly consistent. The precision of replication, with a few exceptions, is not as good with any of the instrument types used in the present study as it was with those obtained by FAAS. This poorer precision may reflect an inherent vari-

Table III. Comparative Analytical Data from the Four Instrumental Methods

		ICPAES[b]		DCPAES[b]		FAFS[b]		FAAS[b]
		HCl	HNO$_3$	HCl	HNO$_3$	HCl	HNO$_3$	HNO$_3$
Barium	$\overline{C}$[a]	0.027	0.039	0.047	0.053	0.050	0.035	
	% RSD	14.6	10.1	4.77	3.52	14.3	12.8	
	LOD	0.018	0.013	0.003	0.007	0.010	0.011	c
	% AD	1.69	0.833	1.26	1.27	1.12	0.591	
Calcium	$\overline{C}$	101.	88.	87.	79.	100.	95.	97
	% RSD	1.22	2.58	9.33	6.15	3.58	5.73	2.80
	LOD	0.060	0.050	0.166	0.147	0.050	0.024	0.143
	% AD	0.404	0.444	0.738	0.620	0.474	0.267	1.01
Copper	$\overline{C}$			0.380	0.332	0.287	0.303	0.33
	% RSD	c	c	8.53	8.57	5.91	6.83	2.37
	LOD			0.025	0.027	0.026	0.028	0.0032
	% AD			0.985	1.03	0.567	0.256	4.98
Iron	$\overline{C}$	1.860	1.30	1.05	0.815	1.06	0.83	0.92
	% RSD	9.20	4.50	16.1	3.40	14.7	11.7	1.83
	LOD	0.267	0.063	0.081	0.068	0.165	0.184	0.0005
	% AD	0.649	0.446	1.24	3.36	2.27	1.68	0.302
Magnesium	$\overline{C}$	142.	119.	97.	103.	121.	110.	115
	% RSD	5.25	5.88	4.07	1.85	4.60	5.60	1.83
	LOD	0.195	0.080	0.151	0.196	0.219	0.187	0.240
	% AD	0.592	0.526	0.514	0.603	1.02	1.02	1.20
Manganese	$\overline{C}$	0.264	0.302	0.161	0.169	0.179	0.180	0.18
	% RSD	3.31	6.53	5.89	6.92	7.54	8.61	3.80
	LOD	0.012	0.012	0.007	0.008	0.028	0.017	0.0020
	% AD	0.203	0.479	1.59	1.28	1.45	2.01	1.76
Potassium	$\overline{C}$	2109.	1652.	2288.	1854.	1818.	1859.	1925
	% RSD	1.54	1.93	4.99	4.94	2.59	4.57	2.43
	LOD	3.39	2.93	1.95	1.03	2.76	2.02	8.36
	% AD	2.16	0.96	1.06	0.21	1.52	2.19	3.78
Rubidium	$\overline{C}$	0.676	0.578	0.442	0.376			
	% RSD	8.13	9.80	4.52	8.84			
	LOD	0.380	0.128	0.043	0.52	c	c	c
	% AD	0.633	0.542	2.596	2.11			
Sodium	$\overline{C}$	11.0	9.64	8.31	5.76	7.03	6.59	5.25
	% RSD	12.4	10.1	4.57	5.55	3.27	3.94	2.22
	LOD	0.037	0.017	0.008	0.005	0.006	0.016	0.0187
	% AD	1.04	0.72	0.516	1.00	0.987	1.40	1.05
Zinc	$\overline{C}$			0.353	0.304	0.294	0.281	0.37
	% RSD			2.94	8.25	15.6	6.85	2.72
	LOD	c	c	0.064	0.076	0.045	0.134	0.0009
	% AD			6.36	5.14	1.13	0.089	1.41

[a] $\overline{C}$ = Average concentration, ppm; % RSD = % Relative Standard Deviation; LOD = Limit of Detection, ppm; % AD = Average Deviation of Measurement. [b] All concentrations are calculated on the basis of single strength orange juice (SSOJ). [c] Values not measured, see text.

ability in the dry ashing sample preparation procedure used in this study. It has been documented quite extensively in the literature that ashing contributes to a number of unavoidable variations in recoveries of elements (18, 19). This probably is not the complete answer since in some instances the average values obtained in this study appear to be somewhat higher than those obtained by FAAS. In spite of the variability noted between some of the methods, the results seem well within similar ranges of concentrations and the degree of conformity establishes considerable confidence in the general validity of the results. It should be pointed out here that an error was discovered in the FAAS values for manganese reported in ref. 1. This error has been corrected for the purposes of inclusions in Table III. With this corrected value, there is remarkable agreement between DCPAES, FAFS, and FAAS values for manganese. The concentration values in Table III have all been calculated on the basis of single strength orange juice to conform to the expressions in ref. 1.

The concentration of sample chosen to analyze most of the trace elements was 10 g of FCOJ (as weight before drying and ashing) to 100 mL of final aqueous solution. This resulted in a solids concentration which was readily aspirated by both the ICPAES nebulizer and the FAFS burner. High solids are generally not a problem with the type of nebulizer used in the DCPAES system described here. The sample concentration also represented a compromise made such that the volume of solutions would be sufficient for completing all the analyses without having to resort to additional ashing. Even so the final volume to sample ratio was smaller in this study than used in the FAAS study. This means that the latter method of measurement most certainly compares well in terms of sensitivity and reproducibility with the newer types of instrumentation at these very low concentration levels.

It was not possible to measure zinc and copper by the ICPAES spectrometric system used by us because of insufficient spectral resolution in our spectrometer which led to spectral interferences and poor signal-to-noise ratios.

Although concentration values are given for barium and rubidium by ICPAES, the values are close to the detection
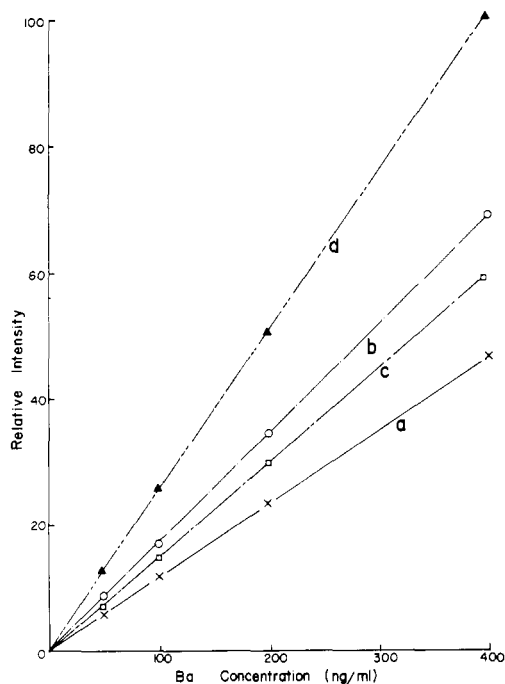
Figure 2. Matrix effects on the calibration curve of barium using DCPAES at the atom line (553.55 nm) and the ion line (455.40 nm). (a) Barium in 0.1 M HNO_3; atom line. (b) Barium in 0.1 M HNO_3 containing 1000 ppm K; atom line. (c) Barium in 0.1 M HNO_3; ion line. (d) Barium in 0.1 M HNO_3 containing 1000 ppm K; ion line

limits for these two elements. The ICPAES detection limits (see following discussion) calculated for barium and rubidium were, respectively, 0.013 and 0.128 ppm and were lower in the nitric matrix than in the hydrochloric acid matrix (See Table III).

No values are given for rubidium using FAFS because the detector used in this instrumental setup was not responsive at the most sensitive wavelength (7800 Å). Also it should be noted that no values appear by FAAS for either barium or rubidium because the need to determine these two elements for fingerprinting purposes in orange juice was not recognized at the time of carrying out that prior study. Furthermore, the instrumentation used in collecting the earlier data was no longer available and thus the data on barium and rubidium could not be obtained.

Detection Limits. Evaluation of what can be termed "practical limits of detection" was made by determining a standard deviation of measurement for each element using

the replicate samples and multiplying the slope of the analytical calibration curve (in linear units) by three standard deviations. It can be seen that there are some disappointing figures of merit for all of the atomic methods for the ashed orange juice matrix used, but especially for the ICPAES spectrometric system used here. In a number of instances, detection limits were orders of magnitude above those expected; the authors attribute this to the influence of the *principal* (relatively highly concentrated) *elements* in this matrix.

Other Observations. With regard to convenience in using the various types of instruments described in this paper, a single operator can most conveniently handle the FAAS or the DCPAES. Because of our particular systems, both the ICPAES and the FAFS were less convenient as far as wavelength selection and sample manipulation. The FAFS system made up for a somewhat inconvenient geometry by contributing the advantages of computerized calculations and readout of data. Data handling operations were performed by a desk calculator (Wang) on the results from both the ICPAES and DCPAES.

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