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Application Note

Measurement of Nutrient and Trace Elements in Juices and Various Food Matrices Using Ultrasonic Nebulization with ICP-AES Detection

Introduction

Consumers have become more concerned about the levels of potentially toxic trace elements such as arsenic, cadmium, and lead in beverages and food. Of specific concern are products intended for consumption by children. Reliable and precise methods of food analysis are important to maintain the safety of the food supply. In addition, accurate data is necessary to comply with food labeling requirements for nutrients such as iron, calcium, sodium, and potassium.

In this application note, various food and juice matrices are analyzed for nutrient and trace elements using an ultrasonic nebulizer with ICP-AES detection. Ultrasonic nebulization offers improved element transport efficiency versus conventional pneumatic nebulizers supplied as standard kit with ICP-AES instruments. Figures of merit will include signal enhancement, calibration, and element detection limits. Of specific interest is improved detection of more difficult elements such as arsenic and lead.

Instrumentation

ICP-AES: PerkinElmer Avio 500

Ultrasonic Nebulizer: Teledyne CETAC U5000AT$^+$

Microwave Digestion System: CEM Mars 6

Experimental Setup

The U5000AT$^+$ ultrasonic nebulizer (USN) was connected to the host ICP-AES via an Ar nebulizer gas line, a sample out line to the ICP torch, and sample tubing from the host peristaltic pump to the ultrasonic nebulizer transducer. No computer control is required for the ultrasonic nebulizer. A picture of the U5000AT$^+$ USN is given in Figure 1.

Figure 1. Teledyne CETAC U5000AT$^+$ Ultrasonic Nebulizer

A comparison of operating conditions is listed in Table 1.

Table 1: Operating Conditions for Standard Nebulizer and U5000AT$^+$ Ultrasonic Nebulizer

Parameter	Standard Setup	U5000AT$^+$ USN
ICP Power	1500 W	1500 W
Plasma Gas	8.0 L/min	8.0 L/min
Auxiliary Gas	0.2 L/min	0.2 L/min
Nebulizer Gas	0.70 L/min	0.62 L/min
Torch injector	2 mm	2 mm
Uptake Rate	1.0 ml/min	1.0 ml/min
Cassette Position	-3.0	-5.0
Resolution	Normal	Normal
Nebulizer Type	Meinhard K	Piezoelectric
Spray Chamber	Baffled cyclonic	Conical
Heater Temp	N/A	120°C
Cooler Temp	N/A	5°C

Calibration

The ICP-AES instrument was calibrated using digested standards prepared in 10% HNO_3 + 4% H_2O_2. The H_2O_2 oxidizes As^{3+} to As^{5+} for improved As recoveries. A minimum of a blank plus three standards is required for calibration. The correlation coefficient for the calibration curve must be greater than 0.998 to be considered valid. A mixing tee was installed before solution introduction to each nebulizer, adding a 100 µg/L yttrium solution for internal standardization. Integration time was 5 seconds with 3 replicates for each blank, standard, and sample analyzed. The calibration ranges, wavelengths, and view type used for analysis are listed in Table 2. For some elements, more than one emission wavelength was used to extend the range of analysis.

Table 2: Calibration ranges and wavelengths

Element	Wavelength (nm)	View	Calibration Range
Calcium	317.933	Radial	0.1-10mg/L
	315.887	Radial	1-100mg/L
Magnesium	285.213	Radial	0.1-10mg/L
Potassium	766.490	Radial	0.1-10mg/L
Sodium	589.592	Radial	0.1-10mg/L
	330.237	Radial	1-100mg/L
Antimony	206.836	Axial	10-1000µg/L
Arsenic	188.979	Axial	10-100µg/L
Barium	493.408	Radial	10-1000µg/L
Beryllium	313.107	Axial	10-1000µg/L
Cadmium	214.440	Axial	10-1000µg/L
Chromium	205.560	Axial	10-1000µg/L
Copper	327.393	Axial	10-100µg/L
Iron	238.204	Axial	50-1000µg/L
Lead	220.353	Axial	10-1000µg/L
Manganese	257.610	Axial	50-1000µg/L
Molybdenum	202.031	Axial	10-1000µg/L
Nickel	231.604	Axial	10-1000µg/L
Phosphorus	178.221	Axial	10-1000µg/L
	214.914	Radial	1-100mg/L
Selenium	196.026	Axial	10-1000µg/L
Uranium	409.014	Axial	50-1000µg/L
Zinc	206.200	Axial	50-1000µg/L

Sample Preparation

For this application, several samples were selected that are representative of a variety of food matrices: 100% cranberry juice, apple juice from a juice box, 100% fruit punch from a juice box, dry cereal, baby food from a pouch, and a donut. In addition, three standard reference materials were analyzed – NIST® 1538 Rice Flour, NIST® 1577 Bovine Liver, and NIST® 1549 Non-Fat Milk Powder. Samples were digested following the procedure outlined in FDA EAM (Elemental Analysis Manual) 4.4[1]. To each digestion vessel, the sample amounts listed in Table 3 were added.

Table 3: Sample weights and volumes for digestion

Sample Type	Amount Digested
NIST® standards	0.5 g
Dry food such as cereal	0.5 g
Wet food such as baby food	1 g
Juice	5 mL

To each digestion vessel 8mL of concentrated HNO_3 and 1mL of 30% H_2O_2 were added. The samples were observed for reaction for at least 10 minutes in a ventilation hood prior to capping and digesting. Sample were digested in a microwave system using the conditions in Table 4.

Table 4: Microwave System Operating Conditions

Power	Ramp	Hold	Temp
1200 W	25 min	15 min	200°C

After digestion was complete, samples were cooled to room temperature and diluted to a final volume of 25mL with 18.2MΩ water.

Results

Instrument Detection Limits

Ten reagent blanks of 10% HNO_3 / 4% H_2O_2 were analyzed using the standard nebulizer and the U5000AT+ Ultrasonic Nebulizer with ICP-AES detection. Instrument detection limits (IDLs) for each nebulizer were calculated by multiplying the standard deviation of the blank concentrations of the 10 replicates by 3. Results for elements of interest are listed in Table 5.

Table 5: Instrument Detection Limits for As, Cd, Pb, Se

Element	IDL Std neb (µg/L)	IDL U5000AT+ (µg/L)	Improvement Factor
Arsenic	5.53	0.35	15.8
Cadmium	0.54	0.10	5.4
Lead	4.97	0.52	9.5
Selenium	7.62	0.97	7.8

Samples and Spikes

Samples were spiked at concentrations of 10 µg/L and 50 µg/L for trace elements and 0.5mg/L for Ca, Na, Mg, and K prior to digestion. As per the EAM[1], spike recovery must be 80-120% to be considered passing. If the analyte concentration was greater than 30% of the spike value, results are not reported.

Juice spike results are listed in Table 6. All results except for selenium in apple juice pass the EAM guidelines. Selenium passed in an apple juice matrix when spiked at 50 µg/L.

Table 6: Per Cent Spike Recoveries in Various Juice Matrices

Element	Cranberry Grape Juice 10 µg/L Spike Recovery %	Apple Juice 10µg/L Spike Recovery %	Apple Juice 50µg/L Spike Recovery %	Fruit Punch 50µg/L Spike Recovery %
Antimony	105	104	104	98
Arsenic	86	107	86	104
Barium	82	96	88	106
Beryllium	101	115	115	99
Cadmium	105	102	105	98
Chromium	98	99	92	84
Copper	107	96	105	96
Iron	-	-	111	107
Lead	97	104	108	92
Manganese	-	-	113	105
Molybdenum	-	-	108	97
Nickel	-	-	113	96
Selenium	103	73	115	86
Sodium	-	-	-	94
Uranium	104	98	88	82

The cranberry/grape juice 10 µg/L spike was measured using both the U5000AT+ ultrasonic nebulizer and the standard pneumatic nebulizer. In the spectra displayed in Figure 2, the U5000AT+ is represented by the green line and the standard nebulizer is represented by the blue line. For As and Pb, a sharp peak is detected on the U5000AT+ spectrum but not on the standard nebulizer spectrum. Per cent recovery for both As and Pb spikes using the standard nebulizer was zero.

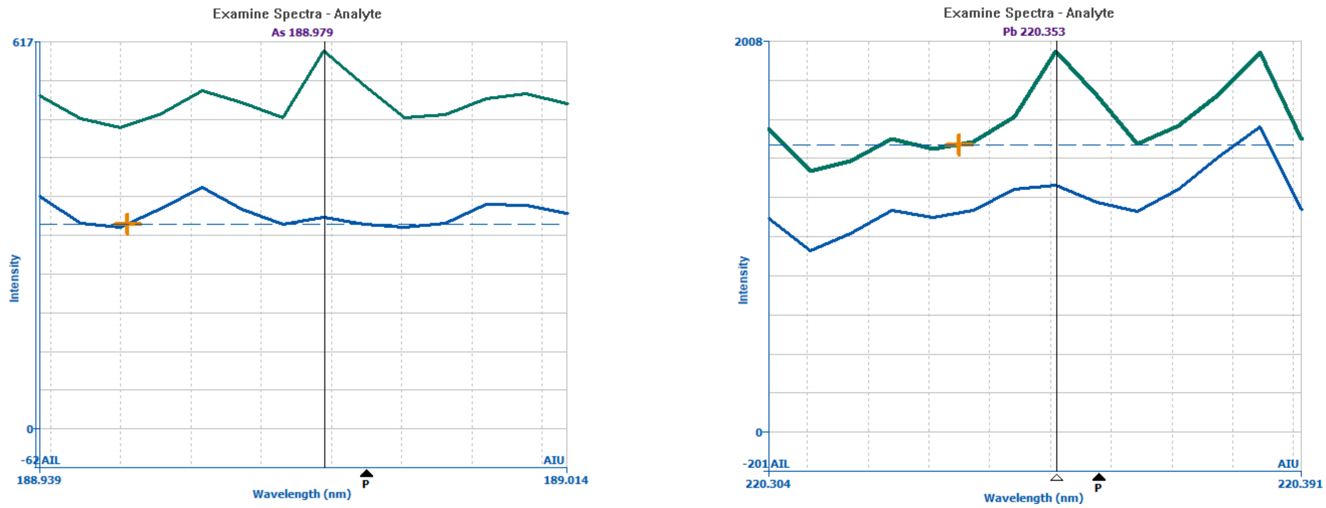

Figure 2. Comparative Spectra for As and Pb Spikes in Cranberry/Grape Juice

Various food matrices were also spiked and analyzed using the U5000AT⁺ USN with ICP-AES detection. Baby food #1 is a blend of apples, carrots, blueberries, and yogurt. Baby food #2 is a blend of bananas, blueberries, and oats. Results are listed in Table 7. All per cent spike recoveries pass except for Se in baby food #1; the failure may be caused by a matrix effect.

Table 7: Per Cent Spike Recoveries in Various Food Matrices

Element	Spike concentration (µg/L)	Baby food #1 spike recovery %	Baby food #2 spike recovery %	Baby rice cereal spike recovery %	Glazed donut spike recovery %	Breakfast cereal spike recovery %
Antimony	50	96	94	99	95	99
Arsenic	50	94	108	101	-	-
Barium	50	88	95	96	106	101
Beryllium	50	97	103	96	111	99
Cadmium	50	98	109	95	111	108
Calcium	500	-	-	-	-	110
Chromium	50	88	95	89	104	104
Copper	50	98	98	101	111	101
Lead	50	91	98	82	97	97
Magnesium	500	-	-	-	-	102
Manganese	50	99	90	117	-	110
Molybdenum	50	95	98	97	110	107
Nickel	50	100	108	95	104	100
Selenium	50	77	99	95	105	91
Sodium	500	-	89	-	-	-
Uranium	50	86	84	96	88	86
Zinc	50	103	117	-	-	-

NIST® Certified Reference Materials

Results for NIST® standard reference materials using the U5000AT+ USN with ICP-AES detection are listed in Table 8. Standards were diluted at a minimum of 50x (digestion dilution). Elements with reference values below the detection limit of the ICP-AES were not reported. According to EAM 4.41, reference values should have a recovery of 80-120% to be considered passing. All per cent recoveries satisfy this requirement.

Table 8: Per Cent Recoveries in Various NIST® Certified Reference Materials

	1577 Bovine Liver			1538 Rice Flour			1549 Nonfat Milk Powder		
Element	Reference Value (mg/kg)	Result (mg/kg)	Recovery %	Reference Value (mg/kg)	Result (mg/kg)	Recovery %	Reference Value (mg/kg)	Result (mg/kg)	Recovery %
Barium	-	-	-	-	-	-	2.2	2.062	94
Cadmium	0.44	0.497	113	-	-	-	-	-	-
Calcium	120	116	97	118	112	95	13000	12245	94
Copper	158	148	94	2.4	2.42	101	-	-	-
Iron	194	186	96	7.4	7.6	102	1.78	1.68	95
Magnesium	600	547	91	560	513	92	1200	1186	99
Manganese	9.9	9395	95	20	19	97	-	-	-
Molybdenum	3.5	3.37	96	1.46	1.43	98	-	-	-
Phosphorus	11100	9477	85	1530	1732	113	10600	9737	92
Potassium	9960	9410	93	1280	1189	93	16900	14694	87
Sodium	2430	2100	86	-	-	-	4970	4679	94
Zinc	123	107	87	19.4	19.3	100	46.1	54.5	118

The bovine liver reference material was analyzed using the standard pneumatic nebulizer and the U5000AT+ USN to compare ICP-AES results. For Cd, no peak was detected at 8.8 µg/L (value of Cd in bovine liver before dilution factor is applied) using the standard nebulizer. The spectra for both nebulizers are shown below in Figure 3: the green line is the spectrum with the U5000AT+ and the blue line is the spectrum with the standard nebulizer. The U5000AT+ enhanced the Cd signal and spike recovery passed at 113%.

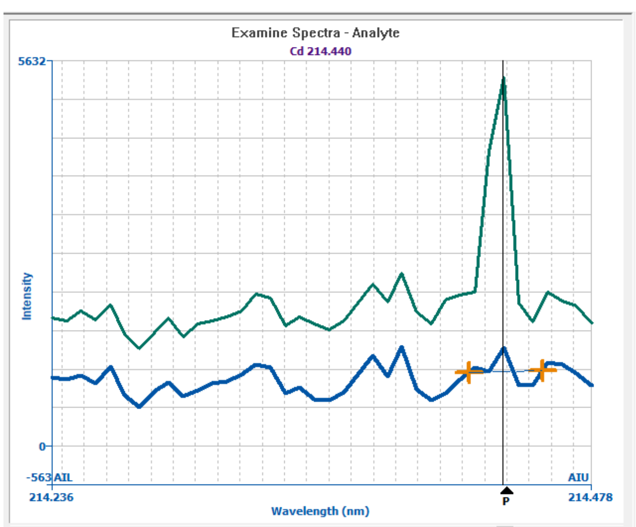

Figure 3. Comparison of Cd ICP-AES Signal for Standard Nebulizer (blue) vs. U5000AT+ Ultrasonic Nebulizer (green)

Conclusions

The U5000AT+ Ultrasonic Nebulizer enhances element signal with ICP-AES so that the difficult elements such as As and Pb can be detected at lower concentrations in a variety of juices and food matrices. The ultrasonic nebulizer / ICP-AES combination is also capable of providing accurate nutrient results necessary for package labels. With the signal enhancement capabilities of the ultrasonic nebulizer, difficult matrices can be diluted at higher amounts and still achieve the required detection limits.

This application note provides data for a limited number of food matrices; the USFDA has done extensive research regarding the use of the ultrasonic nebulizer for analysis of food products. For more information on different matrices and ultrasonic nebulization, refer to EAM 4.4[1] Appendix A.

References

1. Mendak, William R., FDA Elemental Analysis Manual, EAM 4.4 “Inductively Coupled Plasma-Atomic Emission Spectrometric Determination of Elements in Food Using Microwave Digestion” Version 1.1 (August 2010) (www.fda.gov/EAM)

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