Title: ICP-OES Multielemental Analyses of Carbonated Soft Drinks.

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Abstract:

This experiment had only one week where inductively coupled plasma optical emission spectrometry (ICP-OES) was used to conduct multielemental analyses in a bottled sample of Coke Zero, bottled Dasani, QC-5, QC-7, QC-21, 2% HNO_3 rinse and high purity H_2O as the blank. From ICP analysis, it was found that Coke Zero had both Sb and Se in abundance, and Dasani water only had Cd which could be an issue to 21 CFR 165.110. There were also many elements abundant within the samples that were not on the labels including B, Si, and V which the CFR did not have standards for. It was also found for both elements, sodium and potassium, listed on the label were not accurate with sodium having a 84.81% error and potassium having a 19.37% error.

Keywords: inductively coupled plasma optical emission spectrometry, multielemental, abundance, standard, error.

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I. Introduction

We used Inductively coupled plasma optical emission spectrometry (ICP-OES) to determine the concentrations (ppm) of multielements in my Coca-Cola Zero bottled water sample that I purchased from a vending machine located in Busch Student Center by the bus stop. For my pre-laboratory report, Drava et. al.[1] used ICP-OES to determine concentrations of trace elements (As, Cd, Co, Cu, Fe, La, Li, Mn, Ni, P, Pb, Sc, Sn, Sr, V, Y, and Zn), within plant samples. They concluded that a lot of important differences in accuracy and precision were obtained for the studied elements for future experiments. The first additional article that I read, Abdel-Rahman et. al.[2] used ICP-OES to determine concentrations of lead and cadmium in irrigation water, soils and maize grains from different sites in Egypt. The second additional article that I read, Peixoto et. al.[3] used ICP-OES to determine if the contents in bovine milk were about the same in soy-based and if soy-based was a good substitute for bovine milk.

Table 1. My refereed journal articles.

Corresponding Author	**Date Submitted**	**Date Accepted**	**Samples**	**My reference number**
Giuliana Drava	October 30, 2019	December 4, 2019	Plant samples that contained different amounts of trace elements, (As, Cd, Co, Cu, Fe, La, Li, Mn, Ni, P, Pb, Sc, Sn, Sr, V, Y, and Zn)	1
Gomaa N. Abdel-Rahman	June 11, 2019	November 28, 2019	Irrigation water, soils, and maize grains from different sites in Egypt	2
Rafaella Regina Alves Peixoto	July 14, 2019	December 1, 2019	Phosphorus and Zinc in soy-based beverages	3

From pages 1021 to 1027 of the textbook,[4] the theory of Auger electron spectroscopy is explained. Auger electron spectroscopy (AES) is another name for ICP-OES. The Auger process is compared to the XRF process where AES has a higher chance of occurring for elements with lower atomic numbers, but decreases as the atomic number increases. XRF, on the other hand, has a lower chance of occurring for elements with lower atomic numbers, but increases as the atomic number increases. The AES method can detect elements with a sensitivity of 0.5 atom% that ranges from lithium to uranium. Using both XRF and AES combined, plotting the Auger

electron kinetic energy vs. the XPS photon binding yields the chemical states for the specific element being analyzed. Figure 1 below displays the energy level diagram of "Magnesium".

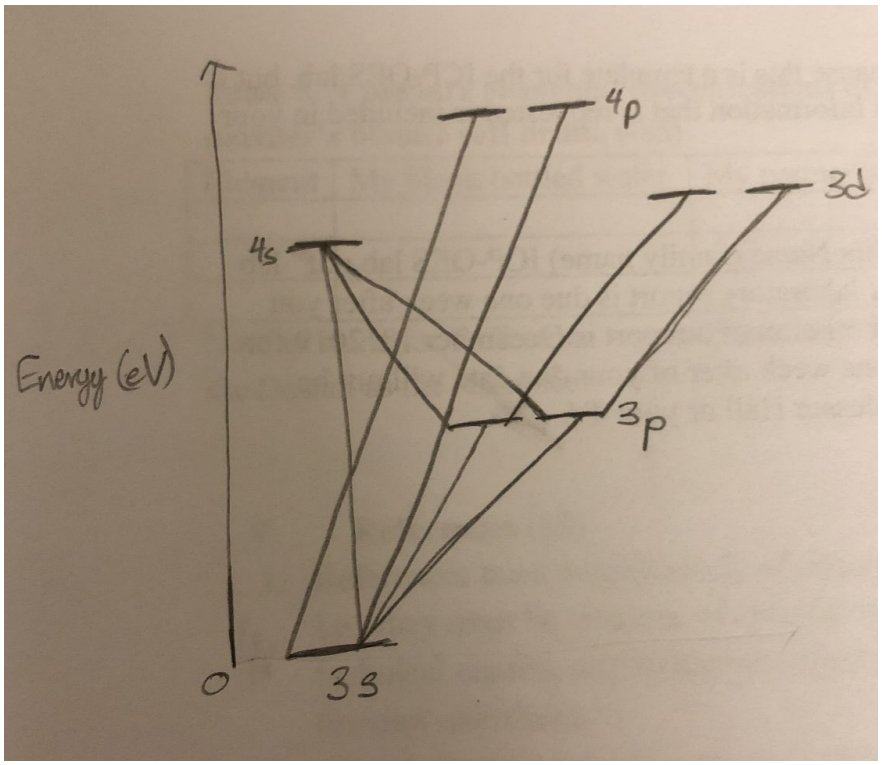


Figure 1. Energy level diagram of Magnesium (Mg).

An equation is stated in page 1021 of the textbook,[4] where it relates fractional atom concentration, line intensity, and atomic sensitivity factor:

$$C_A = \frac{n_A}{\Sigma n_i} = \frac{I_A/S_A}{\Sigma I_i/S_i} \qquad (1)$$

with C_A as the fractional atom concentration, I as the intensity of the line, and S as the atomic sensitivity factor. The equation for correcting a sample intensity is as follows:

$$I_{\text{Not Corrected}} - I_{\text{BLANK}} = I_{\text{CORRECTED}} \qquad (2)$$

where $I_{\text{Not Corrected}}$ is the intensity that is collected without the blank in consideration, I_{BLANK} is the intensity of the blank collected and $I_{\text{CORRECTED}}$ is the intensity corrected by the blank. The next equation used to find the concentration of an element from a standard and its intensities.

$$\frac{Intensity_{sample}}{Intensity_{STD}} * Concentration_{STD} = Concentration_{sample} \qquad (3)$$

where Intensity is the corrected intensities for the respective sample and the concentrations are from the known standard or the one being calculated for the sample element. The fourth equation that is used in the calculation is for percent error:

$$Error = \frac{Accepted - Experimental}{Accepted} * 100 \qquad (4)$$

where accepted is the value in documented tables, and experimental is measured from the experiment. The final equation that was used was to determine the amount of trace elements in the sample compared to what the nutrition label states.

$$Value = \frac{C}{1000mL} * 591\ mL \qquad (5)$$

where value is the amount in milligrams calculated in the sample, C is the concentration found by ICP, and 591 mL is the volume of the drink sample.

Table 2 below states the FDA allowed concentrations of trace elements within bottled water in ppm. These values were obtained from 21 CFR 165.110[5] where it also states that mineral water is allowed to exempt from Cl, Mn, Zn, and Fe maximum concentrations.

Table 2. FDA bottled water elements[5].

Element	**Analytical Wavelength (nm)**	**Maximum Level (ppm)**
Al	396.153	0.2
As	188.979	0.010
Au	267.595	0.1
Ba	233.527	2
Cd	228.802	0.005
Cl	725.67	250
Cr	267.716	0.1
Cu	327.393	1.0
Fe	238.204	0.3
Hg	253.652	0.002
Mn	257.61	0.05
Ni	231.604	0.1
Pb	220.353	0.005
Sb	206.836	0.006
Se	196.026	0.05
Zn	206.2	5.0

II. Experimental

Samples

The sample that was purchased was Coca-Cola Zero from a vending machine within the Busch Student Center near the bus stop and the dining hall entrance. The cost of the black Coca-Cola Zero, 20 fluid ounces (591 mL) sample was $1.75. Figures 2-4 shows the chain of custody form and photograph of the sample analyzed in the laboratory.

Fall 2019 Chemistry 348 Chain of Custody
Carbonated Soft Drink Collection Form. Bring to laboratory with your sample.

Date of collection 12/9/2019 , **time** 3:00 PM EST

Location Busch Student Center Vending Machines by Bus Stop

Collected by Alan Yu **Print Name,**

Alan Yu **Signed**

December 10, 2019 **Date**

Sample description Coca-Cola Zero, 0 Sugar, 0 Calories, Black Label, 591mL

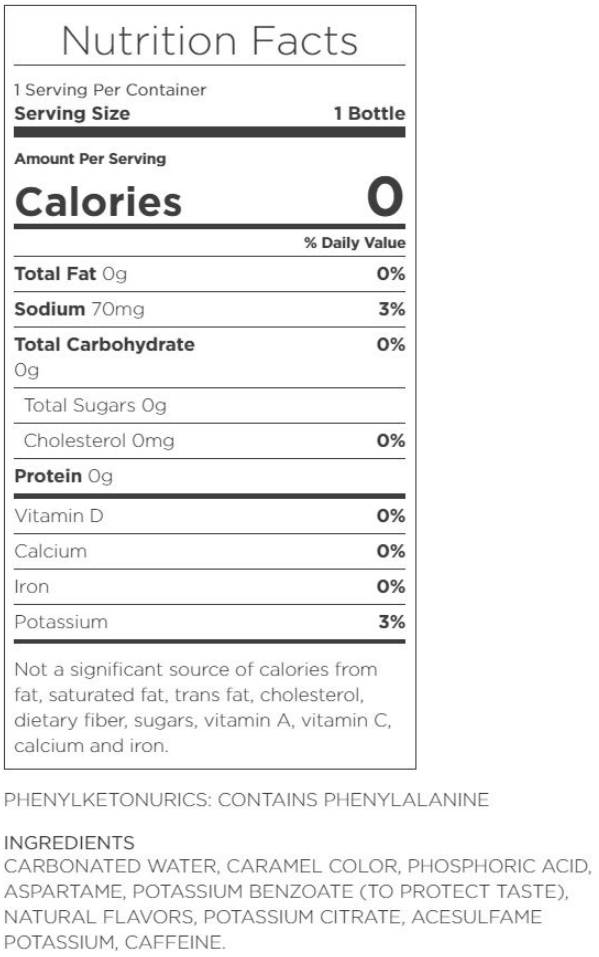
Sample ID Lot number: 4900004086

Sample expiration date: February 17, 2020

Sample manufacture date if any:

Figure 2. Documenting the carbonated soft drink with chain of custody form completed. Sample Lot number is assumed, using label barcode.

Figure 3. Photograph of my carbonated soft drink sample with nutrition fact panel.



Nutrition Facts

1 Serving Per Container

Serving Size **1 Bottle**

Amount Per Serving

Calories **0**

	% Daily Value
Total Fat 0g	**0%**
Sodium 70mg	**3%**
Total Carbohydrate 0g	**0%**
Total Sugars 0g	
Cholesterol 0mg	**0%**
Protein 0g	
Vitamin D	**0%**
Calcium	**0%**
Iron	**0%**
Potassium	**3%**

Not a significant source of calories from fat, saturated fat, trans fat, cholesterol, dietary fiber, sugars, vitamin A, vitamin C, calcium and iron.

PHENYLKETONURICS: CONTAINS PHENYLALANINE

INGREDIENTS
CARBONATED WATER, CARAMEL COLOR, PHOSPHORIC ACID, ASPARTAME, POTASSIUM BENZOATE (TO PROTECT TASTE), NATURAL FLAVORS, POTASSIUM CITRATE, ACESULFAME POTASSIUM, CAFFEINE.

Figure 4. Screenshot of my carbonated soft drink nutrition facts panel from the Coca Cola website.

Materials and Supplies

Baker Instra Analyzed HNO_3 (CAS #: 7697-37-2) was purchased from VWR (Radnor, PA). Acid washed Falcon centrifuge vials 20-mL were purchased from ThermoFisher (Waltham, MA). Spex 21 and Spex 5 trace element standards were purchased from Spex CertiPrep (Metuchen, NJ). Argon, 99.99% purity was purchased from AirGas (Radnor, PA). Dasani (owned by the Coca-Cola Company, Atlanta, GA) bottled water control.

Instrumentation

PerkinElmer Optima 7300-DV ICP-OES spectrometer (Waltham, MA) with PerkinElmer autosampler, controlled by Syngistix by PerkinElmer (Waltham, MA).

Instrument operating parameters are summarized in Table 3.

Table 3. Instrument Operating Parameters.

Parameter	**Value**
Plasma Power RF	1,300 W
Ar Nebulizer Flow	0.8 L/min
Plasma Ar gas flow rate	15 L/min
Ar Auxiliary flow	0.2 L/min
Sample Flow Rate	1 mL/min
Sample Acquisition Time	10 secs
Sample Repeats	3

Table 4-6 summarizes the ICP-OES elements analyzed, element species, and their wavelengths.

Note: For values that were negative in both the blank and the sample itself, the values were changed to zero and omitted from calculating in the tables below.

Table 4. ICP-OES Selected Elements for SPEX 5.

Element	**Line Type**	**Oxidation State**	**Wavelength (nm)**
Ag	I	0	328.068
Al	I	0	396.153
As	I	0	188.979
Au	I	0	267.595
B	I	0	249.677
Ba	II	1	317.933
Ca	II	1	317.933
Cd	I	0	228.802
Co	II	1	228.616
Cr	II	1	267.716
Cu	I	0	327.393
Fe	II	1	238.204
K	I	0	404.721

Table 4. cont. ICP-OES Selected Elements for SPEX 5.

Element	Line Type	Oxidation State	Wavelength (nm)
Mg	I	0	285.213
Mn	II	1	257.61
Na	I	0	589.592
Na	I	0	330.237
Ni	II	1	231.604
Sb	I	0	206.836
Se	I	0	196.026
Si	I	0	251.611
Sr	II	1	407.771
Sr	II	1	232.235
V	II	1	290.88
Zn	II	1	206.2

Table 5. ICP-OES Selected Elements for SPEX 7.

Element	Line Type	Oxidation State	Wavelength (nm)
Ag	I	0	328.068
Al	I	0	396.153
As	I	0	188.979
Au	I	0	267.595
B	I	0	249.677
Ba	II	1	317.933
Ca	II	1	317.933
Cd	I	0	228.802
Cr	II	1	267.716
Cu	I	0	327.393
Fe	II	1	238.204
K	I	0	404.721
Mg	I	0	285.213

Table 5. cont. ICP-OES Selected Elements for SPEX 7.

Element	Line Type	Oxidation State	Wavelength (nm)
Mn	II	1	257.61
Na	I	0	589.592
Na	I	0	330.237
Ni	II	1	231.604
Pb	II	1	220.353
Sb	I	0	206.836
Se	I	0	196.026
Si	I	0	251.611
Sn	II	1	189.927
Sr	II	1	407.771
V	II	1	290.88
Zn	II	1	206.2

Table 6. ICP-OES Selected Elements for SPEX 21.

Element	Line Type	Oxidation State	Wavelength (nm)
Al	I	0	396.153
As	I	0	188.979
B	I	0	249.677
Ca	II	1	317.933
Cd	I	0	228.802
Cl	I	0	725.67
Co	II	1	228.616
Cr	II	1	267.716
Cu	I	0	327.393
Fe	II	1	238.204
Mg	I	0	285.213
Mn	II	1	257.61
Na	I	0	589.592

Table 6. cont. ICP-OES Selected Elements for SPEX 21.

Element	Line Type	Oxidation State	Wavelength (nm)
Na	I	0	330.237
Ni	II	1	231.604
Pb	II	1	220.353
Sb	I	0	206.836
Se	I	0	196.026
Si	I	0	251.611
Sr	II	1	407.771
Sr	II	1	232.235
V	II	1	290.88
Zn	II	1	206.2

Analytical Procedure:

There was only one week for this laboratory experiment. Every individual taking this laboratory course required a different sample of carbonated drink so that no two people analyzed the same drink. Drinks were purchased before the laboratory period started. When the laboratory period started, the drinks were brought into the laboratory and about 10 mL of the drink were poured into a Falcon tube where the sample was swiftly degased. After degassing the sample, the autosampler tray was filled in designated locations where each person placed a sample in a slot. The instrument was rinsed with 2% HNO_3 rinse so that no contaminants could be allowed in the sample analysis. Each individual went up to the machine that had the Syngistix program and ran their own respective samples and the professor ran the QC check, Dasani H_2O, Spex 5, Spex 7, Spex 21, and blank H_2O samples.

III. Results and Discussions

Table 7 summarizes the concentrations of elements in my sample compared to Dasani bottled water. The concentrations were determined using Equation 3 from the introduction:

$$\frac{Intensity_{sample}}{Intensity_{STD}} * Concentration_{STD} = Concentration_{sample} \quad (3)$$

Table 7. ICP-OES Carbonated Soft Drink Trace Element Results

Element	Coke Zero (ppm)	Max Level (ppm)	Dasani Bottle Water (ppm)
Al	0.0106	0.2	NONE
B	0.05	N/A	0.02
Ba	0.01	2	0.0009
Ca	6.96	N/A	0.06
Cd	NONE	0.005	0.005
Cr	0.004	0.1	NONE
Cu	NONE	1.0	0.009
Fe	0.004	0.3	NONE
K	122.78	N/A	1.67
Mg	13.15	N/A	24.27
Mn	0.00007	0.05	0.004
Na	17.99	N/A	1.8
Sb	0.02	0.006	NONE
Se	0.09	0.05	0.01
Si	1.3	N/A	0.09
V	0.02	N/A	0.03
Zn	1.01	5.0	0.00005

From Table 7, there is a plethora of trace elements that are in both Coke Zero and Dasani water that were not listed on the nutrition label. For Dasani water, Cd has a concentration of 0.005ppm which is right on the FDA regulated value of 0.005ppm. For the Coke Zero sample, Sb violates the regulated value of 0.006ppm, and Se violates the value of 0.05ppm. For the other elements, B, Ca, K, Mg, Na, Si, and V had no set values and will be assumed that these elements concentrations are in compliance with 21 CFR 165.110. These could be from the pipes used to transfer liquids, or could even be from the water itself used to make the carbonated drink. These concentrations are not close to what the nutrition label states and many more elements are abundant that they do not report about. Since Cd is in abundance in Dasani water and Sb and Se are in abundance for Coke Zero, these two bottled samples can be said that they do not comply with 21 CFR 165.110.

On the nutrition label it states that there are 70mg of sodium per serving which is one bottle. Using the experimental value, the calculated amount of sodium in the sample is 10.63ppm

which is about 84.81% error from what the label stated. For potassium, there are 90mg potassium per serving and the calculated value was 72.56ppm which gives an error of 19.37%. Since these two are the only elements on the label, I cannot believe the nutrition facts label for my soft drink for both sodium and potassium.

Table 8. QC Check form that is filled out upon request.

QC Check (µg/mL)	Element	Amount Measured (µg/mL)	% Error
nd	Al	0.062	>0%
41.3	As	46.5	12.59%
nd	Ba	0.0	0%
41.0	Ca	43.2	5.37%
40.6	Cd	56.3	27.89%
41.0	Co	47.3	15.37%
40.8	Cr	46.1	12.99%
nd	Cs	0.0	0%
41.7	Cu	42.7	2.40%
40.7	Fe	47.1	15.72%
nd	Hg	0.0	0%
nd	K	0.0	0%
41.0	Mg	63.0	53.66%
41.1	Mn	50.6	23.11%
nd	Na	6.1	>0%
40.9	Ni	46.9	14.67%
nd	P	0.0	0%
41.0	Pb	47.5	15.85%
nd	Rb	0.0	0%
40.7	Sb	46.2	13.51%

Table 8. Cont. QC Check form that is filled out upon request.

QC Check (µg/mL)	Element	Amount Measured (µg/mL)	% Error
41.0	Se	52.2	27.32%
nd	Si	0.9	>0%
nd	Sn	0.0	0%
41.0	Sr	47.6	16.10%
40.8	Ti	0.0	100%
40.7	V	44.5	9.34%
nd	W	0.0	0%
40.7	Zn	45.4	11.55%

IV. Conclusions

Calculating the values for sodium and potassium and comparing to the nutrition label, a 84.81% error for sodium and 19.37% error for potassium was found. This leads to me not being able to believe what the label states about what is promised within the sample per serving. From comparison with 21 CFR 165.110, only Cd was in the dangerous territory of violation in Dasani water, and for Coke Zero Sb and Se were found to be overabundant and violates the CFR.

Table 9. Compared elemental concentrations of my Coke Zero carbonated soft drink with my partner's Mountain Dew (PepsiCo, Purchase, Harrison, NY) carbonated soft drink.

Element	Coke Zero (ppm)	Mountain Dew (ppm)	Difference (ppm)
Al	0.0106	0.0101	0.0005
B	0.05	0.03	0.02
Ba	0.01	0.006	0.004
Ca	6.96	2.95	4.01
Cd	NONE	0.017	-0.017
Cr	0.004	NONE	0.004
Cu	NONE	0.002	-0.002
Fe	0.004	0.013	-0.009

Table 9. cont. Compared elemental concentrations of my Coke Zero carbonated soft drink with my partner's Mountain Dew carbonated soft drink.

Element	Coke Zero (ppm)	Mountain Dew (ppm)	Difference (ppm)
K	122.78	5.06	117.72
Mg	13.15	6.61	6.54
Mn	0.00007	0.004	-0.00393
Na	17.99	83.77	-65.78
Sb	0.02	0.28	-0.26
Se	0.09	2.11	-2.02
Si	1.3	NONE	1.3
Sr	NONE	0.8	-0.8
V	0.02	0.004	0.016
Zn	1.01	NONE	1.01

Based on the difference in ppm column in table 9, my laboratory partner's sample of Mountain Dew had only eight trace elements that were more prevalent compared to mine with ten trace elements that were prevalent. However, since there was an abundance of K and Mg, it could be said that my sample of Coke Zero is potentially more dangerous than that of my laboratory partner's. Based on the amount of elements present in both samples, both drinks had the same amount of electrolytes.

V. References

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