Determination of calcium, magnesium, and potassium in various apple samples using ICP-AES

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Abstract

The mass percentage of calcium, magnesium, and potassium in several apples was determined using inductively coupled plasma atomic emission spectrometry (ICP-AES). The apples tested include: golden delicious, jonagold, braeburn, fuji, red delicious, granny smith, gala, and pink lady. The results show that in general, all apples tested had magnesium and potassium concentrations within the natural range. Calcium concentrations were higher due to the addition of a calcium chloride solution on the apple.

Introduction

Apples are a commonly chosen inexpensive and healthy snack for the "on-the-go" college student. Depending on the season the apples may be fresh or previously refrigerated.[1] Of the apples that are refrigerated several of them are likely to develop a condition known as "Bitter Pit"; this is classified by small abrasions on the outside surface of the apples that cover portions of the fruit that become brown and spongy with a signature bitter taste.[2]

The condition is known to affect all apple varieties. The vulnerability of a particular apple to "Bitter Pit" has been found to be proportional to the amount of calcium present in the given sample.[2,3] If the concentration of calcium in the apple is greater than 30 mg/kg it is unlikely to develop Bitter Pit, however if the concentration is lower than 19 mg/kg it is considered very likely to contract the condition at some point.[1] In the event that the concentration is between the bounds of 19 – 30 mg/kg, the importance of the concentrations of magnesium and potassium becomes apparent; the ratios of calcium/potassium and calcium/magnesium represent a balanced relationship of minerals that serves as an indicator to whether the apple may be spared from the condition.[1]

A balanced relationship indicates that the apple can be stored and is less likely to encounter Bitter Pit. For a relationship to be balanced the ratio of the concentrations in mg/kg for calcium: magnesium must be greater than 0.6, and the ratio of calcium: potassium multiplied by 10 must be greater than 0.17.[1]

Typical concentrations of the analytes found in apples are as follows: calcium 10-50 mg/kg, magnesium 25-50 mg/kg, and potassium 500-1500 mg/kg.[1] The concentrations of the analytes are found to depend mostly on the type of apples used, so the dependence is genetic in nature. Because of the wide ranges in the typical concentrations for the analytes the most common technique for determination is inductively coupled plasma atomic emission spectrometry (ICP-AES), this is due to the linear nature of the light-emission over large ranges of concentrations.[1]

In this experiment, ICP-AES was used for the determination of calcium, magnesium, and potassium concentration in a variety of apple samples.

Experimental

The method was followed according to Duxbury in *Determination of Minerals in Apples by ICP-AES.*[1]

Sample Preparation

From each of the apples purchased at Hornbacher's, three 1-g samples were taken. The samples were placed in separate 250-mL beakers. Aliquots of trace metal grade concentrated nitric acid (Sigma-Aldrich) were added successively to the sample. While heating with a hotplate, the sample was brought to about 250°C in the fume hood after the first 15-mL aliquot of nitric acid was added. The sample was allowed reach near dryness before adding the 10-mL aliquot, and then the heating was repeated. Once the sample was fully digested, the beaker was set aside to cool. After cooling, the solution was filtered through Whatman 540 Ashless Filter Paper into a 100-mL volumetric flask and diluted with distilled water.

Standard Preparation

A total of four standards were prepared from purchased 1000-ppm stock solutions of calcium (PlasmaCAL), magnesium (Ricca) and potassium (Ricca). The final concentrations of the standards were: 0.25, 0.50, 0.75, 1.00 ppm for calcium and magnesium, and 5.00, 10.0, 15.0, 20.0 ppm for potassium. Standard concentrations were chosen because the natural range fell within these values.

ICP-AES Conditions

The ICP-AES used was a Varian 715-ES model. The conditions were: plasma power 1.20 kW; plasma argon flow 15.0 L/min; auxiliary argon flow 1.5 L/min; nebulizer pressure 200 kPa; photomultiplier tube voltage 650 V. The wavelengths analyzed were calcium (422.673 nm), potassium (766.490 nm), and magnesium (285.213 nm). The instrument took the average of three samples with an uptake every 15 seconds.

Results and discussion

Calibration Plots

Calibration plots were created using Microsoft Excel and the data given from the ICP software. From these calibration curves, the mass percent of each mineral along with the standard deviation was calculated.

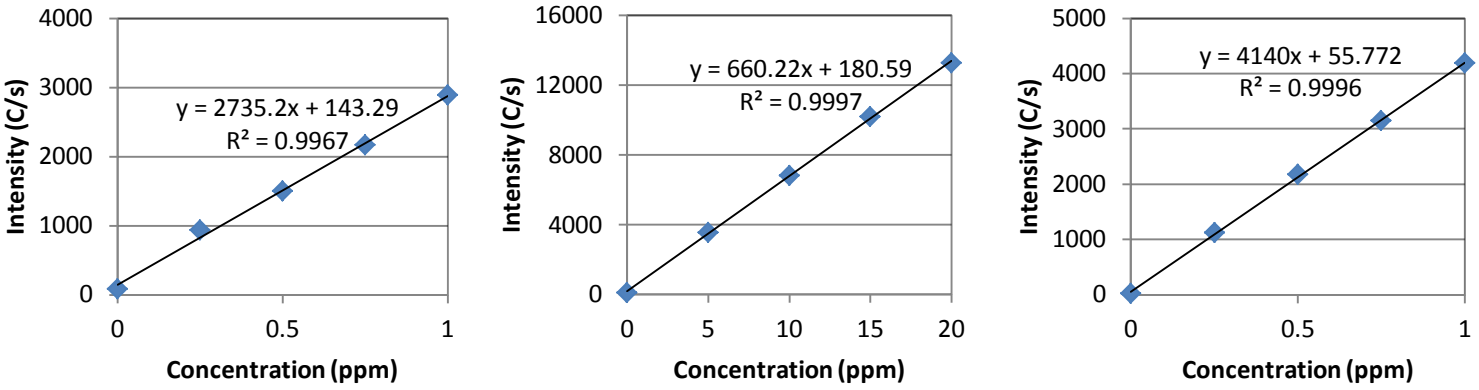

Figure 1. Calibration curves of calcium (left), potassium (middle), and magnesium

Table 2. Determination of calcium concentration in various apple samples along with standard deviation.

Apple	n	Average [Ca] (mg/kg)	Standard Deviation	%RSD
Braeburn	3	110	20	18
Gala	3	87	9	10
Granny Smith	3	80	30	38
Golden Delicious	2	71	4	5
Pink Lady	3	70	7	10
Red Delicious	3	69	8	12
Fuji	3	46	7	15
Jonagold	3	28	4	13

Table 3. Determination of potassium concentration in various apple samples along with standard deviation.

Apple	n	Average [K] (mg/kg)	Standard Deviation	%RSD
Pink Lady	3	1200	200	17
Red Delicious	3	1100	50	4.5
Braeburn	3	970	50	5.2
Gala	3	900	18	2
Granny Smith	3	900	200	22
Fuji	3	900	200	22
Golden Delicious	2	820	10	1.2
Jonagold	3	690	40	5.8

Table 4. Determination of magnesium concentration in various apple samples along with standard deviation.

Apple	n	Average [Mg] (mg/kg)	Standard Deviation	%RSD
Pink Lady	3	44	5	11
Jonagold	3	40	10	25
Golden Delicious	2	35	2	5.4
Braeburn	3	34	3	8.5
Granny Smith	3	32	3	8.8
Fuji	3	31	3	8.8
Red Delicious	3	30	2	8.3
Gala	3	29	1	3.8

As shown in Table 1, Table 2, and Table 3, magnesium and potassium concentrations fell within the range of 29-44 mg/kg and 690-1200 mg/kg, respectively. The accepted range for these minerals is 25-50 mg/kg and 500-1500 mg/kg, which our data supports. Calcium concentrations fell within the range of 28-110 mg/kg. These concentrations were above the accepted natural value range of 10-50 mg/kg, but this is an acceptable range because apples purchased from a supermarket tend to have a calcium chloride solution on the outside to enhance the cold storage ability of the fruit.[1]

The balanced mineral ratios for the various mineral samples, shown in Table 5, were within the acceptable range due to the large increase in calcium concentration which was attributed to the addition of a calcium chloride solution on the outside of the apple. Therefore, since every sample had a mineral ratio above the minimum value, each of the samples may be stored with low probability of procuring the bitter pit condition.

Table 5. Mineral ratios for the various samples

Apple	Ca/Mg	Ca*10/K	Apple	Ca/Mg	Ca*10/K
Braeburn	3.2	1.1	Golden Delicious	2	0.87
Gala	3	0.97	Pink Lady	1.6	0.58
Granny Smith	2.5	0.89	Fuji	1.5	0.51
Red Delicious	2.3	0.63	Jonagold	0.69	0.4

Comparisons between the various samples showed that the largest concentrations of calcium were found in Braeburn (110 mg/kg), Gala (87 mg/kg), and Granny Smith (80 mg/kg). The largest magnesium concentrations were Pink Lady (44 mg/kg), Jonagold (38 mg/kg), and Golden Delicious (35 mg/kg). Potassium was most concentrated in Pink Lady (1200 mg/kg), Red Delicious (1100 mg/kg), and Braeburn (970 mg/kg).

Conclusions

It was determined by ICP-AES that due to the presence of a calcium chloride solution additive the calcium concentrations in all samples except Jonagold were well above 33 mg/kg, which makes them low probability of contracting bitter pit upon cold storage.

The balanced mineral ratios of the Jonagold samples were greater than the minimum ratios presented by Duxbury which helps conclude that Jonagold, along with all varieties of apples tested are not at risk of the bitter pit condition if refrigerated.

Acknowledgments

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References

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