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The pH and Titratable Acidity of Still and Sparkling Flavored Waters: The Effects of Temperature and Storage Time

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Abstract

Statement of the problem: Flavored waters have become increasingly popular in the Trinidadian retail market. There is a paucity of literature on the erosive potential of these products on dental hard tissue. Purpose: This study 1) evaluated the pH and titratable acidity of popular still and sparkling flavored waters in the Trinidadian marketplace and 2) evaluated the effect of time and temperature on pH and titratable acidity. Materials and methods: A calibrated pH meter was used to measure pH at baseline (T_0), at one week of storage (T_1) and at one month of storage (T_2). Titratable acidity was determined using 0.1 M sodium hydroxide until a neutral pH of 7 was attained. Results: All tested flavors of both still and sparkling water demonstrated pH well below the critical pH of 5.5. Reduced temperature and time in storage caused varying degrees of change in both pH and titratable acidity. Generally, the largest changes in titratable acidity occurred for sparkling varieties of water. Conclusion: The still and sparkling flavors of water tested are potentially very erosive to dental hard tissue.

Keywords

pH, Titratable Acidity, Flavored Water, Dental Erosion

1. Introduction

Several beverages, including fruit juices, colas, energy and sports drinks, have been shown to have a deleterious effect on teeth, specifically due to the erosive potential of these drinks on dental hard tissue [1]. Dental erosion is the irreversible loss of hard tissues by chemical means, not associated with microbial activity

[2]. Erosion is normally initiated when hydrogen ions interact with apatite crystals of dental enamel [3]. When considering the erosive potential of beverages, both pH and measurements of titratable acidity have been widely reported.

While pH can be measured easily, this measurement only gives an indication of initial hydrogen ion dissociation in tested beverages, but gives no information regarding concentrations of non-disassociated acid within a beverage [4]. Titratable acidity is a more precise indicator of the total acidic concentration of tested beverages, with many researchers concluding that titratable acidity of beverages is a more accurate measure of erosive potential on dental hard tissue [5] [6]. *In-vitro* studies of titratable acidity demonstrate the ability of a buffering agent, in most instances OH ions to neutralize all available acid. Tenuta *et al.* stated that titratable acidity is responsible for the time that salivary pH is maintained at low levels [7]. The greater the buffering capacity of a beverage, the longer it will take for saliva to neutralize acids within beverages [8].

Other factors, such as the presence and saturation of calcium [6], fluoride [8] and phosphate ions [9], may influence the erosive potential of beverages. The presence of chelating agents and buffers may also influence dental hard tissue erosion once exposure occurs. The temperature of beverages on consumption can also affect dissolution of dental hard tissue since colder temperatures affect the acid dissociation constant [6]. Acidic beverages that are not chilled are more likely to be associated with increased erosive potential [8].

Flavored water can often be perceived by consumers to be a healthy alternative to colas, energy and sports drinks [10]. The erosive potential of such drinks, however, is largely unknown due to a paucity of literature on the topic. Awareness of the erosive potential of new formulations of beverages, introduced into retail markets, should be closely monitored to educate consumer choices. Water is a beverage that may be consumed over a long period of time at either room temperature or chilled. In the absence of specific labelling instructions, water may be also refrigerated, once opened and consumed at a later date. There is a paucity of literature on the effects of temperature and time on the pH and titratable acidity of beverages, particularly flavored waters. We hypothesized that effect of temperature and time would not be simple due to the presence of preservatives, buffering and chelating agents and various other additives in retail flavored bottled waters.

The aim of this study was to determine the effect of temperature and storage time on the pH and titratable acidity of still and sparkling flavored waters found in the Trinidadian retail market. Our null hypothesis stated that there would be no difference in the pH and titratable acidity as a result of variations in temperature and storage time.

2. Materials and Methods

The flavored waters, together with their ingredients, used in this study are listed in **Table 1**. Plain still and sparkling bottled waters were used as positive controls.

Table 1. Brand, Flavor and Ingredients of tested waters.

BRAND	FLAVOR	INGREDIENTS
Oasis	**Cran Water**	Water, Sugar, Cranberry and Red Grape Juice Concentrates, Natural Flavours, Sodium Hexametaphosphate, Citric Acid, Malic Acid, Tartaric Acid, Potassium Sorbate & Sodium Benzoate, Natural Ginseng Extract, Natural Carmel Colour, Calcium Disodium EDTA, Amaranth Red
	Mixed Berry	Water, Sugar, Red Grape Juice Concentrates, Natural and Artificial Flavours, Sodium Hexametaphosphate, Citric Acid, Cranberry Juice Concentrate, Malic Acid, Tartaric Acid, Potassium Sorbate & Sodium Benzoate, Natural Ginseng Extract, Calcium Disodium EDTA, Amaranth Red, FD&C Blue #1 & Yellow #5
	Plain Water	Purified Water, Magnesium Sulphate, Sodium Bicarbonate, Potassium Chloride
Blue Waters	**Cran Apple**	Water, Sugar, Citric Acid, Natural Flavour, Malic Acid, Sodium Hexametaphosphate, Sodium Benzoate & Potassium Sorbate, Vegetable Juice Concentrate, Caramel Colour, Sucralose, Panax Ginseng Root Extract, Calcium Disodium EDTA, Amaranth Red, Vitamin A, Vitamin E
	Cran Lime	Water, Sugar, Citric Acid, Natural Flavour, Malic Acid, Sodium Hexametaphosphate, Sodium Benzoate & Potassium Sorbate, Vegetable Juice Concentrate, Caramel Colour, Sucralose, Panax Ginseng Root Extract, Calcium Disodium EDTA, Amaranth Red, Vitamin A, Vitamin E
	Cranberry (Cran +)	Water, Sugar, Citric Acid, Natural Flavour, Malic Acid, Sodium Hexametaphosphate, Sodium Benzoate & Potassium Sorbate, Vegetable Juice Concentrate, Caramel Colour, Sucralose, Panax Ginseng Root Extract, Calcium Disodium EDTA, Amaranth Red, Vitamin A, Vitamin E
	Sparkling Cran Apple	Carbonated Water, Sugar, Citric Acid, Natural Flavour, Malic Acid, Sodium Hexametaphosphate, Sodium Benzoate & Potassium Sorbate, Vegetable Juice Concentrate, Caramel Colour, Sucralose, Panax Ginseng Root Extract, Calcium Disodium EDTA, Amaranth Red, Vitamin A, Vitamin E
	Cran Grape	Water, Sugar, Citric Acid, Malic Acid, Sodium Hexametaphosphate, Sodium Benzoate & Potassium Sorbate, Natural Flavour, Vegetable Juice Concentrate, Caramel Colour, Sucralose, Panax Ginseng Root Extract, Calcium Disodium EDTA, Amaranth Red, Vitamin A, Vitamin E
Viva	**Pomegranate Blueberry**	Carbonated Water, Apple Juice Concentrate, Natural Pomegranate and Blueberry Flavours, Citric Acid, Potassium Benzoate and Potassium Sorbate, Acesulfame Potassium, Green Tea Extract, Sucralose, Magnesium Sulphate, Inositol, Calcium Disodium EDTA, Niacinamide, FD&C Blue #1, Calcium D-Pantothenate, Pyridoxine Hydrochloride
	Strawberry Melon	Carbonated Water, Apple Juice Concentrate, Citric Acid, Natural Strawberry and Melon Flavours, Potassium Benzoate and Potassium Sorbate, Sucralose, Green Tea Extract, Acesulfame Potassium, Magnesium Sulphate, Inositol, Calcium Disodium EDTA, Niacinamide, FD&C Red #40, Calcium D-Pantothenate, Pyridoxine Hydrochloride

Continued

Viva	**Orange Mango**	Carbonated Water, Apple Juice Concentrate, Citric Acid, Potassium Benzoate and Potassium Sorbate, Green Tea Extract, Sucralose, Acesulfame Potassium, Natural Orange and Mango Flavours, Gum Acacia, Ester Gum, Calcium Disodium EDTA, Magnesium Sulphate, Inositol, FD&C Yellow #6, Niacinamide, Calcium D-Pantothenate, FD&C Yellow #5, Pyridoxine Hydrochloride
	Black Raspberry	Carbonated Water, Apple Juice Concentrate, Malic Acid, Natural Black Raspberry Flavours, Potassium Benzoate and Potassium Sorbate, Sucralose, Green Tea Extract, Acesulfame Potassium, Magnesium Sulphate, Inositol, FD&C Red #40, Calcium Disodium EDTA, Niacinamide, Calcium D-Pantothenate, Pyridoxine Hydrochloride, FD&C Blue #1
	Peach	Carbonated Water, Apple Juice Concentrate, Citric Acid, Natural Peach Flavours, Potassium Benzoate and Potassium Sorbate, Green Tea Extract, Acesulfame Potassium, Sucralose, Magnesium Sulphate, Inositol, Calcium Disodium EDTA, Niacinamide, Calcium D-Pantothenate, FD&C Yellow #6, Pyridoxine Hydrochloride, FD&C Red #40,
Dasani	**Apple**	Water, Citric Acid, Malic Acid, Natural Flavours, Potassium Sorbate and Sodium Benzoate, Sodium Citrate, Aspartame, Acesulfame K, Sodium Polyphosphate, EDTA, Caramel Colour, Phenylketonurics: Contains Phenylalanine
	Portugal	Water, Citric Acid, Malic Acid, Sodium Polyphosphate, EDTA, Natural Flavours, Sodium Benzoate and Potassium Sorbate, Sodium Citrate, Aspartame, Acesulfame K, Colours Yellow #6 and Red #40. Phenylketonurics: Contains Phenylalanine
	Lime	Water, Citric Acid, Malic Acid, Natural Flavours, Sodium Polyphosphate, EDTA, Sodium Benzoate and Potassium Sorbate, Sodium Citrate, Aspartame, Acesulfame K, Colour Yellow #5. Phenylketonurics: Contains Phenylalanine
	Grapefruit	Water, Citric Acid, Malic Acid, Sodium Polyphosphate, EDTA, Natural Flavours, Sodium Benzoate and Potassium Sorbate, Sodium Citrate, Aspartame, Acesulfame K, Colour Yellow #6 and Red #40. Phenylketonurics: Contains Phenylalanine
	Plain Water	Purified Water, Mineral Salts
Sparkling Ice	**Orange Mango**	Carbonated Water, Citric Acid, Orange Juice Concentrate, Natural Flavour, Gum Arabic, Vegetable Juice, Potassium Benzoate, Sucralose, Beta Carotene, Ester Gum, Green Tea Extract, Calcium Disodium EDTA, Biotin, Niacinamide, Calcium Pantothenate, Vitamin A, Vitamin B12, Vitamin D3, Pyridoxine Hydrochloride
	Pink Grapefruit	Carbonated Water, Citric Acid, Grapefruit Juice Concentrate, Natural Flavours, Potassium Benzoate, Gum Arabic, Sucralose, Vegetable Juice, Ester Gum, Green Tea Extract, Calcium Disodium EDTA, Biotin, Niacinamide, Beta Carotene, Vitamin A, Calcium Pantothenate, Vitamin B12, Vitamin D3, Pyridoxine Hydrochloride
San Pellegrino Terme	**S. Pellegrino**	Carbonated Mineral Water

A double junction glass electrode pH meter was used (Oakton pH150 Oakton Instruments) to record pH. Prior to pH readings, the pH meter was calibrated against a buffering solution containing deionized water, sodium phosphate dibasic, potassium phosphate monobasic, sodium chromate and potassium dichromate (Orion Research Incorporated). All bottled water was analyzed, at room temperature of 25˚C, directly as the water was opened. Fifty milliliter of each flavor of water was used for testing. Two pH readings were taken per bottle and an average found (T_0). The titratable acidity (TA) was determined using 0.1 M sodium hydroxide (NaOH) until a neutral pH of 7 was attained. A magnetic stirrer (Thermolyne Cimarec 3, LabWorld Group) was used to ensure proper mixing of each sample with sodium hydroxide. Each bottled water was tightly recapped and placed in the refrigerator for storage at 19˚C. pH and titratable acidity testing was repeated at one week (T_1) and at one month later (T_2).

TA was calculated using the following formula:

$$\frac{V_{base} \times C_{base} \left(\text{mmol/L}\right)}{V_{sample}}$$

where; V_{base} is the volume of the base used to attain a pH of 7, C_{base} is the concentration of NaOH used and V_{sample} is the volume of the sample used.

The differences in TA, as a product of storage time and temperature, from T_0 to T_1 to T_2 were expressed as a percentage change relative to the T_0 reading, using the formula:

$$\frac{\left(T_1 \text{ or } T_2\right) - T_0}{T_0} \times 100\%$$

All percentage changes were rounded and expressed as whole numbers.

3. Results

The results of pH and titratable acidity at T_0 are shown in **Table 2**. All the tested water demonstrated pH values below critical pH of 5.5.

At one week of storage at 19˚C (T_1), there were positive increases in pH for all the tested waters, except Cran Grape, Pomegranate Blueberry, Strawberry Melon and the control samples of plain bottled water. Measurements of TA ranged from 0 to 0.09 mmol/L with percentage changes ranging from 0 to 300%. These are shown in **Table 3**.

The pH, TA and percentage change in TA at one month (T_2) are shown in **Table 4**.

4. Discussion

The pH results for the investigated flavored waters varied widely with those of other investigators, with pH values being lower than reported values for flavored waters [3] [11]. In fact the results of pH demonstrated in this study are lower than the pH of common energy and sports drinks [3] [6]. Low pH has been discussed as one of the main determinants of the erosive potential of beverages.

Table 2. The mean pH and titratable acidity of tested waters at T_0 (TA-titratable acidity, mmol/L). Flavors denoted with * indicates flavored sparkling. Bottled plain and sparkling water were used as controls).

BRAND NAME	FLAVOR	pH	TA
Oasis	Cran Water	1.82	0.03
Blue Waters	Mixed Berry	1.93	0.02
	Cran Apple	1.81	0.03
	Cran Lime	1.81	0.03
	Cran Berry	1.82	0.03
	Cran Grape	1.88	0.03
	Cran Apple*	1.89	0.03
	Plain Water	5.66	0.00
Viva	Pomergrante Blueberry*	2.11	0.03
	Strawberry Melon*	1.97	0.04
	Orange Mango*	1.83	0.04
	Black Raspberry*	1.96	0.04
	Peach*	1.92	0.03
Dasani	Apple	2.08	0.05
	Portugal	2.64	0.05
	Lime	1.89	0.07
	Grapefruit	1.87	0.08
	Plain Water	4.11	0.00
Sparkling Ice	Orange Mango*	1.84	0.04
	Pink Grapefruit	1.70	0.05
S. Pellegrino	Sparkling Water*	4.35	0.01

Beverages which contain citrates together with a low pH may have an even greater erosive potential since citrates chelate with the calcium of fluoro and hydroxyapatite facilitating a greater erosive effect [8]. The tested flavors of Dasani and Sparkling Ice all contain citrate in their formulations.

Acids, either in the form of natural juices or as additives are added to beverages to counteract the taste of sugar and serve as preservatives since they prevent bacterial overgrowth [12]. These acids are normally organic acids such as citric, tartaric and malic acid. Of the locally produced or bottled brands Oasis and Blue Waters brands contained sugar with either the citric, malic acid or tartaric acid used to counteract the taste of sugar. Flavors of Dasani had no added sugar but both citric and malic acid added.

Other brands such as Viva had additives such as apple juice which naturally contains malic acid which gives a characteristic tartness to the beverage. The tested flavors of Sparkling Ice had both added citric acid and additives of citrus fruits such as orange or grapefruit concentration which also contains naturally

Table 3. The mean pH and titratable acidity of tested waters at T_1 (TA-titratable acidity, mmol/L). Flavors denoted with * indicates flavored sparkling. Bottled plain and sparkling water were used as controls).

BRAND NAME	FLAVOR	pH	% CHANGE (from T_0)	TA	% CHANGE (from T_0)
Oasis	Cran Water	1.84	2	0.03	0
Blue Waters	Mixed Berry	2.00	4	0.03	0
	Cran Apple	1.91	6	0.03	0
	Cran Lime	1.85	2	0.03	0
	Cran Berry	1.87	3	0.03	0
	Cran Grape	1.97	−2	0.04	33
	Cran Apple*	1.84	4	0.03	0
	Plain Water	5.61	1	0.00	0
Viva	Pomergrante Blueberry*	2.11	0	0.04	33
	Strawberry Melon*	1.97	0	0.07	75
	Orange Mango*	1.91	4	0.09	125
	Black Raspberry*	1.97	1	0.08	100
	Peach*	1.95	2	0.08	167
Dasani	Apple	2.15	3	0.05	0
	Portugal	2.69	2	0.05	0
	Lime	1.92	3	0.07	0
	Grapefruit	1.97	5	0.08	0
	Plain Water	5.59	0	0.00	0
Sparkling Ice	Orange Mango*	1.78	3	0.07	75
	Pink Grapefruit	1.78	5	0.08	60
S. Pellegrino	Sparkling Water*	4.19	2	0.04	300

occurring citric acid.

Reddy *et al.* proposed a chemical erosive potential scale based on the pH values of extrinsic dietary acids and their associated potential to dissolve apatite crystals [3]. Based on this scale all the still and sparkling flavored waters in this study would be classified as extremely erosive while the plain bottled sparkling water, would be classified as minimally erosive. During experimentation both brands of still bottled water showed a sharp increase in pH with miniscule volumes of NaOH, demonstrating a relatively low titratable acidity.

Increases in pH measurements after one week in storage are indicative of a sustained hydrogen ion concentration which can be available for apatite dissolution. This led the authors to conclude that once the water was opened and stored, temperature was not the only factor at play in affecting hydrogen ion dissociation. Conversely for the Viva Cran Grape where there was a decrease in the pH, reduction in ambient temperature was the most important factor in

Table 4. The mean pH and titratable acidity of tested waters at T_2 (TA-titratable acidity, mmol/L). Flavors denoted with * indicates flavored sparkling. Bottled plain and sparkling water were used as controls).

BRAND NAME	FLAVOR	pH	% CHANGE (from T_0)	TA	% CHANGE (from T_0)
Oasis	Cran Water	1.91	5	0.03	0
Blue Waters	Mixed Berry	1.97	2	0.03	50
	Cran Apple	1.88	4	0.03	0
	Cran Lime	1.84	2	0.03	0
	Cran Berry	1.88	3	0.03	0
	Cran Grape	2.00	2	0.03	0
	Cran Apple*	1.92	6	0.03	0
	Plain Water	5.60	−1	0.00	0
Viva	Pomergrante Blueberry*	2.11	0	0.03	0
	Strawberry Melon*	2.00	2	0.05	25
	Orange Mango*	1.89	3	0.06	50
	Black Raspberry*	2.00	2	0.05	25
	Peach*	1.95	2	0.05	67
Dasani	Apple	2.16	4	0.05	0
	Portugal	2.74	4	0.05	0
	Lime	2.05	9	0.07	0
	Grapefruit	1.99	6	0.09	13
	Plain Water	4.82	17	0.00	0
Sparkling Ice	Orange Mango*	1.88	2	0.06	50
	Pink Grapefruit	1.80	6	0.05	0
S. Pellegrino	Sparkling Water*	5.27	21	0.01	0

dissociation of hydrogen ions. The exact concentrations of the various acidic components in each flavor and their associated dissociation mechanics could play a role in the overall pH changes that were observed. Formulations with higher concentrations of citric acid, a polyprotic acid with 8 hydrogen ions available for dissociation would likely have higher pH values over time. In those brands and flavors of water where the pH values continued to rise even at one month, this is indicative of continued hydrogen ion dissociation.

Titratable acidity or the buffering capacity has been less valued as a predictor of the erosive potential of extrinsic beverages due to the limited contact of time beverage would have in contact with dental hard tissue. Modified patterns of drinking such as "swish and swallow", particularly with carbonated beverages, could put beverages in contact with hard tissue for longer periods of time making TA more relevant as a predictor of erosive potential [6]. TA, however, is also a measurement of the ability of a beverage to maintain low pH over time and the cancelling effect of salivary buffers [5]. There was a marked increase in the TA of the majority of sparkling or carbonated varieties of flavored waters and the plain sparkling water as a result of storage for one week at 19˚C. This change could be due to breakdown of buffers within the beverages, change in carbon dioxide concentrations or even possibly fermentation due to contamination once the bottle was opened.

With respect to carbon dioxide concentrations this is surprising since once a bottle is opened diminished levels of carbon dioxide would be present, negatively affecting partial pressure and causing a solution that is closer in pH and TA to plain water. The authors assumed that even though bottles of water were opened, over one week the concentration of dissolved carbon dioxide increased. In fact the pH for plain sparkling water increased by 2% at T_1 and 21% at T_2. This is significant, even though carbonic acid is considered a weak acid it has been shown to reduce the surface microhardness of enamel [13]. Weak acids also have the capacity for hydrogen ion dissociation once protons are consumed in the dissolution process [7] [12].

At T_2, the percentage change in TA for some of the sparkling flavors of bottled water in various brands were still higher than compared to values at T_0, however not as high as T_1 values, this is possibly due to a reversal of carbon dioxide dissolution once the bottles had been opened a second time and a reduction of partial carbon dioxide pressure, reducing total carbonic acid concentrations and approximating TA values closer to that of plain water.

The authors however interpreted these findings with caution due to the methodological limitations of the study. Since alterations in temperature directly affect the pH and the acid dissociation constant, it is not possible to confirm if the differences observed between T_0, T_1 and T_2 for both pH and TA were promoted by the time after opening the bottle , the difference in the temperature in which the measures were performed or a combination of both these factors.

Recent research has demonstrated an erosive effect of sparkling flavored waters on human enamel samples [14]. Further research will involve the difference in erosive potential on sparkling versus still flavored waters on both enamel and dentine samples. Additionally other physio chemical properties; such as calcium, phosphate and fluoride concentrations and viscosity should be ascertained since they also play a role in determining the erosive potential of beverages. Finally, the in-vivo effect of these beverages on the buffering capacity of saliva should be examined in an attempt to understand the exact nature of protective salivary buffers when beverages with such low pH values are consumed.

5. Conclusions

Within the limitations of the study, the following conclusions can be drawn:

1) The still and flavored sparkling waters tested in this study may be considered potentially erosive based on the low pH values observed.

2) In general, after one week of storage, pH values continued to increase for

the flavored varieties of still and sparkling flavored water.

3) Sparkling varieties of flavored water showed the largest increases in TA after one week of storage.

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Conflicts of Interest

None of the named authors have any proprietary interests in any of the products used in this study.

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