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Determination of pH, total acid, and total ethanol in oral health products: oxidation of ethanol and recommendations to mitigate its association with dental caries

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Abstract

Acidity contributes to the development of dental caries. The source of this acidity is often attributed to sugar fermentation by endogenous bacteria in the mouth, or to acidic foods and drinks, which lower salivary pH[1]. Paradoxically, oral health mouthwashes may also cause dental caries[2], largely due to the inclusion of ethanol (EtOH/"alcohol") as an antiseptic agent, which can be oxidized to acetic acid. However, the potential deleterious effect of these mouthwashes has not been adequately assessed, nor have the chemical changes in pH and total ethanol been evaluated over time. Here we present data demonstrating changes to pH, total acid, and total ethanol in several popular mouthwashes over time. These changes increase acidity and thus demonstrate an increased risk of dental caries. Finally, we evaluate the chemical mechanism of these changes, and propose preventable solutions.

Introduction

According to previous studies by dental professionals, acidic/low pH beverages and mouthwashes can cause dental demineralization and erosion[1, 3]. These studies have demonstrated that significant loss of enamel can occur within the first few minutes of contact with such acidic solutions[3-5]. This study investigates the chemicals in mouthwashes, and the chemical reactions that cause the decreased pH of mouthwashes over time. We measured changes in the amounts of ethanol, total acid, and pH of the mouthwashes over time. And, here we present data demonstrating changes to pH, total acid, and total ethanol in several popular mouthwashes over time. These changes are mainly caused by ethanol in the mouthwashes, which is often used as an antiseptic agent by Medical and Dental professionals[2]. However, the use of ethanol in the mouthwashes without the proper concentration of antioxidants results in the oxidation of ethanol, resulting in the production of acetic acid, and increased risk of dental erosion. Here we also evaluate the risks posed by these mouthwash formulations and propose recommendations to mitigate these risks.

Materials and Methods

The relationship among pH, total acid, and total ethanol in popular oral health products was determined and the association of these products to dental caries was assessed using standard methods[6-7]. Oral health products were obtained over the counter. For each product, the pH was determined using an ion-selective electrode on date of purchase and after a period of 30 days.

The total acid in solution for each product was determined via acid-base titration on date of purchase and after 30 days. Titration pump was used to deliver titrant solutions. The pump tube was calibrated and placed into a 10 mL graduated cylinder (with 1/10 mL markings) containing the titrant. The pump and timer were run for 300 seconds to measure the volume added and calculate the delivery rate in mL/second. The pH meter was calibrated using 7.0 and 10.0 buffer solutions. Titrant was run through the pump tube for approximately 5 minutes prior to sample analysis. While the titrant was flushing, the sample was prepared by pipeting 30 mL of the sample into a 50 mL beaker containing a stir bar, and continuously stirred plate. The pH probe was rinsed, blotted dry, lowered into the sample, and allowed to sit for 5 minutes for the pH signal to stabilize. Afterwards, the pump tube was introduced into the sample, and the pump and timer were then started. The timer and pump were stopped and the time was recorded when the pH meter read the correct value listed below.

SMW, GMW, LMW	7.6 equivalence point
LWR, GWR	8.7 equivalence point
Crest Pro	7.0 equivalence point

The volume delivered was determined from the time recorded and the Normality of the titrant. This amount equals the H+ in solution at the equivalence point.

$[H^+]$ (mg H^+/L) = (time (s) x flow rate of pump (mL/sec) x N of titrant (meq/mL) x (1 mg H^+/meq)) / volume of sample (mL)

Note that the titration was required to last between 2 and 10 minutes. If titration lasted longer, some or all of the following adjustments were changed: volume of sample, flow tube, and/or the concentration of the titrant. Suggested Concentrations of NaOH (titrant) were as follows and were made from 1.0 M NaOH stock solutions:

LWR	.3000 M
GMW, GWR	.0500 M
SMW, Crest Pro	.0020 M
LMW	.0008 M

The total ethanol in solution for each product was determined via internal standard calibration using headspace Gas Chromatography and mass spectral analysis and compared to the printed total ethanol value on listed ingredients[7]. Standard solutions of various %(wt) ethanol were prepared in deionized water. 125 mL isopropanol was added to each sample at various %(wt). Approximately 0.400 g NaCl was also added to each of the standards to increase the ionic strength of the solution, thus increasing the concentration of analytes in the vapor phase (headspace). Samples of "unknown" ethanol concentration were prepared from 3 popular mouthwashes. 0.400 g NaCl and 125 mL isopropanol were added to 875 mL of each mouthwash. Ethanol concentration in mouthwash was determined by internal standard calibration using headspace gas chromatography and mass spectral analysis. All solutions were heated to 42^{o}C in a sand bath prior to GC/MS analysis. 50uL of headspace was sampled from each vial and injected onto the GC column. The instrumental parameters were as follows: GC column flow=1mL/min helium, 50:1split, 45^{o}C isothermal oven, column=30mx0.25mm DB-5. The mass spectrometer was set to scan from 18-200m/z.

Results

Sample pH, total acid, and total ethanol were measured at the date of purchase and after a period of 30 days. We found that pH and total ethanol decreased as total acid increased in all three samples. Tables 1 shows pH and total acid values for the three sample mouthwashes and Table 2 shows the mean total acid change in the three mouthwashes. There was a direct relationship between mouthwash sample Δ pH and Δ total acid concentration. The sample with the largest Δ pH (LMW; -.29) exhibited the largest changes in total acid concentration (LMW; -14.4%). For all three samples, the mean initial total acid concentration was statistically different from the mean final acid concentration ($p<0.05$, *t*-test). This relationship between mouthwash sample Δ pH and Δ total acid concentration was consistent across all three samples of mouthwash. Table 3 shows the change in percent of total ethanol for the three mouthwash samples. The percent of total ethanol for all three samples decreased between measurements (Table 3). As above, there is a direct relationship between decreased total ethanol and Δ pH and Δ total acid, e.g. the sample with the largest change in total ethanol (LMW; -13.89%) exhibited the largest change in pH (-.29) and total ethanol (-14.4). Thus, over time, each of the three samples exhibit decreases in total ethanol that is accompanied by concomitant increases in total acid and lowered pH.

Table 1. pH and Total Acid in Oral Health Products

Mouthwash	Initial pH	Final pH	ΔpH	Initial Total Acid	Final Total Acid	Δ Total Acid
LMW	4.56	4.27	-.29	0.0089	0.0094	$+5.0 \times 10^{-4}$
SMW	6.71	6.51	-.20	0.0078	0.0081	$+3.0 \times 10^{-4}$
RMW	5.65	5.58	-.07	1.97×10^{-4}	2.0467×10^{-4}	$+3.0 \times 10^{-6}$

Table 2. Mean (± SD) Total Acid in Oral Health Products

Mouthwash	Mean Initial Total Acid	Mean Final Total Acid	% Δ Total Acid
LMW	32.13 (± .72)	17.73 (± .04)	-14.4
SMW	20.45 (± .09)	11.74 (± .08)	-8.71
RMW	12.97 (±.02)	9.54 (± 1.19)	-3.43

Table 3: Total Ethanol

Oral Health Product	Initial	Final	Δ total EtOH	% Error
LMW	31.31%	17.42%	-13.89%	35.24%
SMW	20.71%	11.50%	-9.21%	23.33%
RMW	13.45%	9.57%	-3.88%	14.09%

Discussion

We have demonstrated changes in pH, total acid, and total ethanol in common mouthwashes. The use of ethanol (EtOH/"alcohol") without proper amounts of antioxidants decreases pH of mouthwashes below 5. The chemical mechanism for the oxidation of ethanol to acetic acid is as follows[8]:

$$C_2H_5\text{-}OH + [O] \rightarrow CH_3CHO + [O] \rightarrow CH_3 - COOH$$

ethanol + [O] → ethanal + [O] → ethanoic acid (acetic acid)

Low pH mouthwashes can cause dental caries, because the dominant calcium-containing compounds ("crystals") in the teeth/enamel, calcium phosphate, and hydroxyapatite can dissolve in low pH[2]. Previous studies have demonstrated convincingly that such acidic conditions in solution can lead to significant enamel loss within the first few minutes of contact[3, 5, 9]. Such a timeframe is within the duration of most mouthwash regimens[10-11]. The dissolution of these calcium-containing compounds causes tooth demineralization/erosion and dental caries[2-5, 9-11], and it would be of interest for future studies to determine the possible effects on bacterial growth[1, 4, 5].

In order to mitigate the effects of erosion, previous studies have typically recommended increases in dental care with fluoridated solutions and changes in tooth brushing regimens that include mouthwashes[4, 12]. However, due to the present results, which demonstrate the erosive potential of common mouthwashes, we recommend the following steps to mitigate any problems associated with their use:

1. Addition of chemicals that keep mouthwashes above pH 6. This is necessary, because it has been demonstrated that pH less 5.5 at the surface of the tooth leads to a net loss of enamel and mineral structure on the tooth's surface[2, 4-5, 10]. This can increase the incidence of dental caries[1, 5]. Such dental caries have previously been shown to be mainly caused by the frequency of acid exposure[2, 3, 9, 11]. Some chemicals that increase pH of the mouthwashes are the strong base-producing salts: $Ca^{2+}/Na^{+}/K^{+}$-containing salts, etc.

2. The proper concentration of antioxidants for the ethanol-containing mouthwashes should be used to prevent and reduce the oxidation of the alcohol to acetic acid.

3. Chronic use of alcohol should be discouraged because it can increase the incidence of cancer of the mouth.

4. The establishment of proper dental-care education to protect consumers from dental caries, and promotes dental health.

5. We recommend that mouthwash manufacturers routinely check the change of pH of the mouthwashes, and use preservatives that maintain desirable pH homeostasis in the products.

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