Determination of Calcium Carbonate in Toothpastes

1. Introduction

During one of our IB Chemistry classes, we performed a back titration on an egg shell to determine the amount of calcium carbonate in it. Personally, I found that performing back titration was quite simple and interesting, and I decided to do something similar for my investigation. After researching online about the uses of this compound, I came to know that it is an important ingredient commonly used in toothpastes. So, I started examining the ingredients of various commercial toothpastes available in local markets. From further research, I also came to know that it is an abrasive ingredient, and the abrasives such as dehydrated silica gels and hydrated aluminium oxides give the toothpaste its cleaning power. These abrasives remove food debris and dirty stains on our teeth, and reduce the formation of plaque, hence preventing tooth decay and gum diseases. However, excessive use of abrasives in toothpastes can also cause problems, such as tooth sensitivity due to the thinning of enamel, and the discolouration of teeth. Therefore, I resolved to find how much of this mineral is used in our commercial toothpastes, and how the amount of this mineral varies in different brands of toothpastes, which led to the formation of my research question.

2. Research Question

How does the amount of calcium carbonate vary in five different brands of toothpastes available in local Coimbatore markets?

3. Hypothesis

From information online, I found that the abrasiveness of toothpastes is measured by an index named Radioactive Dentin Abrasiveness – RDA. Pepsodent had a value of 150 RDA, much higher compared to other brands such as Colgate – 68 and Close Up – 80. Hence I hypothesised that Pepsodent would also have higher amounts of $CaCO_3$ compared to other brands, as it is one of the essential abrasives in a toothpaste. The RDA of other local toothpaste brands were unavailable online.

4. Background Information

The most common method used to calculate the concentration of an acid or alkali is by a neutralisation reaction, and the concentration of the other reagent is known. This experimental technique is known as acid-base titration. It is performed by taking a precise volume of alkali using a pipette in a conical flask, and adding the controlled volume of acid from a burette gradually until the equivalence point is reached, where both reactants have exactly neutralised each other. This point can be determined by adding a drop of indicator to the conical flask, such as phenolphthalein, which is colourless in acidic solutions and pink in basic solutions. Calcium carbonate is a weak, insoluble base which reacts with acids to produce salt, water and carbon dioxide. Direct acid-base titration cannot be done with $CaCO_3$ in toothpaste because it is a weak base, and the reaction is very slow when it is close to the endpoint, hence the equivalence point would be difficult to observe. Another reason is that $CaCO_3$ is an insoluble base, therefore it is not an alkali. Instead, a similar experimental technique called back titration can be performed, where a known volume and concentration of an acid is taken in excess to react with all of the $CaCO_3$ in a known volume of toothpaste solution, and then titrating the remaining acid which did not react with a known concentration and controlled volume an alkali in a burette, to determine the volume of the unreacted acid. For my experiment, I decided to take 10 cm^3 of 0.5M HCl as the acid, and 0.5M of NaOH in the burette as the alkali.

$NaOH (aq) + HCl (aq) \longrightarrow NaCl (aq) + H_2O (l)$

From the difference between the volume of the HCl initially added in excess and the volume of unreacted HCl, the volume of acid which reacted with $CaCO_3$ can be found, and subsequently the number of moles of the reacted acid will be equal to the number of moles of $CaCO_3$ as seen from the equation:

$$CaCO_3\,(s) + 2HCl\,(aq) \longrightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)$$

5. Experimental Variables

Independent Variable	• Different brands of toothpaste
Dependent Variable	• Amount of calcium carbonate
Controlled Variables	• Mass of toothpaste taken – approximately 1.0 g • Concentration of NaOH – 0.5M • Concentration of HCl – 0.5M • Volume of HCl addedfor each trial – 10 cm^3 • Volume of NaOH in burette • Total volume of toothpaste solution prepared – 100cm^3 • Volume of toothpaste solution taken for each trial – 20cm^3 • Temperature of solution when heated – 80˚C
Uncontrolled Variable	• Colour of toothpastes

6. Apparatus and Materials

• 5 toothpastes of different brands • Watch glass • 0.5M Hydrochloric Acid • 0.5M Sodium Hydroxide • Distilled Water (Wash bottle) • Electronic balance • Electric heater • Laboratory thermometer	• Burette • Volumetric pipettes – 10cm^3 and 20cm^3 • 100cm^3 Volumetric flask • Measuring cylinder – 500cm^3 and 10cm^3 • Glass funnel • Glass rod • Phenolphthalein

6.1 Uncertainties

Uncertainty of electronic balance = Least count = ± 0.001 g

Uncertainty of thermometer = ½ x Least count = ½ x 1˚C = ± 0.5˚C

Uncertainty of burette = ½ x Least count = ½ x 0.10 cm^3 = ± 0.05 cm^3

Uncertainty of 10 cm^3 pipette = ± 0.02cm^3

Uncertainty of 20 cm^3 pipette = ± 0.06 cm^3

Uncertainty of 100 cm^3 volumetric flask = ± 0.1 cm^3

Uncertainty of 500 cm^3 measuring cylinder = ± 2.5 cm^3

Uncertainty of 10 cm^3 measuring cylinder = ± 0.2 cm^3

7. <u>Methodology</u>

7.1 Preparation of 0.5M NaOH

In order to prepare 0.5M of NaOH, I measured 500 cm^3 of distilled water using a 500 cm^3 measuring cylinder, and added it into a plastic container. Then, I weighed 10.0 g of NaOH pellets using the electronic balance. By adding 10.0g of NaOH to 500 cm^3 of distilled water, and after stirring thoroughly with a stirring rod, 500 cm^3 of NaOH of approximately 0.5M concentration was produced, and it was stored in the labelled plastic container. In order to determine the exact molarity of the NaOH, I had to standardise the NaOH solution prepared using oxalic acid as a primary standard.

7.1.1 Standardisation of NaOH using Oxalic acid as a primary standard

To determine the actual concentration of NaOH prepared, I had to carry out titration with 0.5M oxalic acid of molar mass 126.07 g/mol. In order to prepare exactly 0.5M concentration of the acid, I precisely weighed 6.30 g of oxalic acid crystals. Next, I added the oxalic acid crystals into a half filled volumetric flask with distilled water, and shook well to completely dissolve the crystals. Then, I filled the flask with distilled water up to the 100 cm^3 mark to produce exactly 0.5M concentration of oxalic acid. Afterwards, I titrated the acid prepared against the

NaOH solution. I took exactly 20cm^3 of NaOH using a pipette, in a conical flask and added a drop of phenolphthalein, which turned the solution pink. Following that, I filled a burette with 0.5M oxalic acid, and recorded the initial reading of the acid. Subsequently, I carried out titration with NaOH, shaking the beaker gently as the acid is added to the NaOH. Once the solution had turned from pink to colourless, I stopped the titration, and recorded the final reading of acid in the burette. I carried out this titration for two more trials to determine the average volume of acid used.

Table 1: Titration readings of oxalic acid against NaOH

Trial no.	**Initial reading / cm^3 (± 0.05)**	**Final Reading / cm^3 (± 0.05)**	**Volume added / cm^3 (± 0.1)**
1	0.6	10.4	9.8
2	11.0	20.8	9.8
3	21.0	30.8	9.8

Average volume of acid used = (9.8 ± 0.1) cm^3

Using the average volume of acid used, I calculated the exact molarity of NaOH prepared.

$H_2C_2O_4 + 2NaOH \longrightarrow Na_2C_2O_4 + 2H_2O$

Number of moles = Volume x Concentration

No. of moles of $H_2C_2O_4$ x 2 = No.of moles of NaOH

$V_1M_1 \times 2 = V_2M_2$

$9.8\ cm^3 \times 0.5\ M \times 2 = 20\ cm^3 \times M_2$

$4.9 \times 2 = 20 \times M_2$

$M_2 = 0.49\ M$

7.1.2 Uncertainty Propagation

Uncertainty of concentration of oxalic acid = (0/0.05 + 0.1/100) x 0.5 = ± 0.0005 M

Uncertainty of volume of oxalic acid = ± 0.1 cm^3

Uncertainty of volume of NaOH = ± 0.06 cm^3

Uncertainty of concentration of NaOH = {[(0.1/9.8 + 0.0005/0.5) x 4.9 x 2] ÷ 9.8 + (0.06/20)} x 0.49 = 0.00696 ≈ ± 0.007

The exact molarity of NaOH prepared is (0.490 ± 0.007) M

7.2 Preparation of 0.5M Hydrochloric acid

To produce 0.5M HCl from concentrated HCl of 11.65M concentration, I had to calculate the amount of concentrated HCl needed to produce 500 cm^3 of 0.5M HCl.

$$V_1M_1 = V_2M_2$$
$$V_1 \times 11.65 = 500\ cm^3 \times 0.5$$
$$V_1 = 21.459\ cm^3$$
$$\approx 21.5\ cm^3$$

I measured 478.5 cm^3 of distilled water using 500 cm^3 and 10 cm^3 measuring cylinders in a beaker, and added into a plastic container. Then, I measured 21.5 cm^3 of concentrated HCl using a pipette and graduated syringe, and added the acid to the distilled water to produce 500 cm^3 HCl of approximately 0.5M concentration, which was stored in the labelled plastic container.

7.2.1 Standardisation of HCl using Sodium Hydroxide as a primary standard

To determine the exact molarity of HCl prepared, the acid had to be titrated against the standardised NaOH. I followed the exact same procedure as in 7.1.1 to titrate the NaOH, but with the HCl prepared instead of oxalic acid.

Table 2: Titration readings of HCl against NaOH

Trial no.	Initial reading / cm^3 (± 0.05)	Final Reading / cm^3 (± 0.05)	Volume added / cm^3 (± 0.1)
1	1.0	19.2	18.2
2	17.1	35.2	18.1
3	28.3	46.4	18.1

Average volume of acid used = (18.2 + 18.1 + 18.1) ÷ 3 = (18.1 ± 0.1) cm^3

Using the average volume of acid used, the exact molarity of HCl prepared can be calculated using the equation: $HCl + NaOH \longrightarrow NaCl + H_2O$

No. of moles of NaOH = No.of moles of HCl

$$V_1M_1 = V_2M_2$$

$$20.0\ cm^3 \times 0.49\ M = 18.1\ cm^3 \times M_2$$

$$M_2 = 9.8 / 18.1$$

$$M_2 = 0.5414$$

$$\approx 0.54\ M$$

7.2.2 Uncertainty Propagation

Uncertainty of concentration of NaOH = ± 0.007 M

Uncertainty of volume of acid = ± 0.1 cm^3

Uncertainty of volume of NaOH = ± 0.06 cm^3

Uncertainty of concentration of HCl = (0.06/20 + 0.007/0.490 + 0.1/18.1) x 0.54

= 0.0123 ≈ ± 0.01M

The exact molarity of HCl prepared is (0.54 ± 0.01) M

7.3 Procedure for the experiment

After I had prepared and standardised the reagents HCl and NaOH, I began my actual experiment with the Pepsodent Germicheck+ toothpaste. First, I weighed about 1.0g of the toothpaste using the electronic balance and a watch glass, and recorded the exact mass taken. Then, I transferred the toothpaste sample from the watch glass into a beaker using a glass rod, and added about 50 cm^3 of distilled water to the beaker. I washed back the remaining toothpaste on the watch glass into the beaker using distilled water, and stirred thoroughly to produce a toothpaste solution. Following that, I transferred the toothpaste solution into a 100 cm^3 volumetric flask, and added distilled water to fill up to the 100 cm^3 mark. I closed the flask with its lid and inverted it a few times. Afterwards, I transferred 20cm^3 of toothpaste solution into a beaker using the 20cm^3 pipette, and pipetted out 10cm^3 of HCl to the beaker using the 10cm^3 pipette, and swirled the beaker thoroughly. Then, using the electric heater, I heated the solution to 80˚C, checking the temperature of the solution using a thermometer, to speed up the reaction, and to ensure that all

$CaCO_3$ in the toothpaste solution reacts with the acid. Before heating, I had inserted a glass funnel in the beaker to prevent any loss of acid or solution. After that, I allowed the solution to cool for 5 minutes, washed the sides of the glass funnel with distilled water back into the beaker, and transferred the contents into a conical flask. Next, I added one drop of phenolphthalein indicator to the flask, and it was colourless when added. Afterwards, I filled a burette with NaOH, previously rinsed with NaOH, and recorded down the initial reading. I then back titrated the unreacted acid in the conical flask by adding NaOH from the burette gradually, until the phenolphthalein changed colour from colourless to pale pink. After the titration was done, I recorded down the final volume of NaOH in the burette. I pipetted out 20 cm^3 of the same toothpaste solution from the volumetric flask again into a beaker, and carried out the exact same procedure for another two trials of titration. Eventually, I repeated the entire procedure for 4 other brands of toothpastes: Colgate® Calci-Lock Protection, Dabur Meswak, CloseUp Deep Action and K.P Namboodiri's, performing a total of 15 titrations.

8. Safety and Precautions

For preparation of 0.5M hydrochloric acid, I handled concentrated HCl with utmost care, as it is a highly corrosive chemical. Before taking the concentrated HCl from the storage cabinet, I wore protective equipment, such as eye goggles, chemical-resistant gloves and a lab coat. The measuring of concentrated HCl and adding it to the distilled water was carried out in an operating fume cupboard, to remove toxic vapour from the concentrated HCl. When preparing the dilute solution, I added the concentrated acid to the water, and not vice versa, to prevent the splattering of acid. The reagents prepared were dilute, of concentration 0.5M, hence the disposal of these reagents after the experiment did not cause any environmental hazard to the local surroundings. Also, when using the electric heater, I ensured that I never left it unattended.

9. Data collection

Table 3: Precise mass of different toothpaste samples

Toothpaste	Mass of sample / g(± 0.001)
PepsodentGermicheck +	1.043
Colgate® Calci-Lock Protection	1.027
Dabur Meswak	1.019
CloseUp Deep Action	1.012
K.P Namboodiri's	1.081

Table 4: Titration readings of excess HCl with toothpaste solution

Toothpaste	Initial / cm^3 (± 0.05)	Final / cm^3 (± 0.05)	Volume / cm^3 (± 0.1)
Pepsodent Germicheck+	0.1	6.4	6.3
	6.5	13.1	6.6
	13.5	19.9	6.4
Colgate® Calci-Lock Protection	17.5	25.9	8.4
	26.1	34.6	8.5
	34.6	43.1	8.5
Dabur Meswak	22.4	30.3	7.9
	30.9	38.5	7.6
	36.3	43.8	7.5
CloseUp Deep Action	14.7	26.0	11.3
	24.5	35.1	10.6
	34.8	45.6	10.8
K.P Namboodiri's	25.9	36.4	10.5
	36.0	46.8	10.8
	25.4	36.3	10.9

10. Data Processing

From the 3 trials of titration done for each brand of toothpaste, I have taken the average of the volume of NaOH used and presented below in table 10.1

Table 5: Average volume of NaOH titrated for each toothpaste solution

Toothpaste	Average volume of NaOH / cm^3 (± 0.1)
Pepsodent Germicheck+	(6.3+6.6+6.4) ÷ 3 = 6.4
Colgate® Calci-Lock Protection	(8.4+8.5+8.5) ÷ 3 = 8.5
Dabur Meswak	(7.9+7.6+7.5) ÷ 3 = 7.7
CloseUp Deep Action	(11.3+10.6+10.8) ÷ 3 = 10.9
K.P Namboodiri's	(10.5+10.8+10.9) ÷ 3 = 10.7

From the volume of NaOH titrated, the volume of excess HCl (V_1) can be determined from the equation: NaOH (aq) + HCl (aq) ⟶ NaCl (aq) + H_2O (l)

V_1 = Volume of NaOH x Concentration of NaOH ÷ Concentration of HCl

V_1 = Volume of NaOH x 0.49M ÷ 0.54M

Volume of HCl reacted with $CaCO_3$ (V_2) = Volume of acid taken (10.0 cm^3) – V_1

Number of moles of reacted HCl = V_2 in dm^3 x Concentration of HCl (0.54M)

$CaCO_3$ (s) + 2HCl (aq) ⟶ $CaCl_2$ (aq) + CO_2 (g) + H_2O (l)

No. of moles of HCl ÷ 2 = No. of moles of $CaCO_3$

Table 6:

Toothpaste	Volume of excess HCl / cm^3	Volume of HCl reacted / cm^3	No. of moles of HCl reacted / mol	No. of moles of $CaCO_3$ / mol
Pepsodent Germicheck+	5.8 (± 0.3)	4.2 (± 0.3)	0.002680 (± 3 x 10^{-6})	0.001340 (± 2 x 10^{-6})
Colgate® Calci-Lock Protection	7.7 (± 0.3)	2.3 (± 0.3)	0.001240 (± 3 x 10^{-6})	0.000620 (± 2 x 10^{-6})
Dabur Meswak	7.0 (± 0.3)	3.0 (± 0.3)	0.001620 (± 3 x 10^{-6})	0.000810 (± 2 x 10^{-6})
CloseUp Deep Action	9.9 (± 0.4)	0.1 (± 0.4)	0.000054 (± 4 x 10^{-6})	0.000003 (± 2 x 10^{-6})
K.P Namboodiri's	9.7 (± 0.4)	0.3 (± 0.4)	0.000162 (± 4 x 10^{-6})	0.000081 (± 2 x 10^{-6})

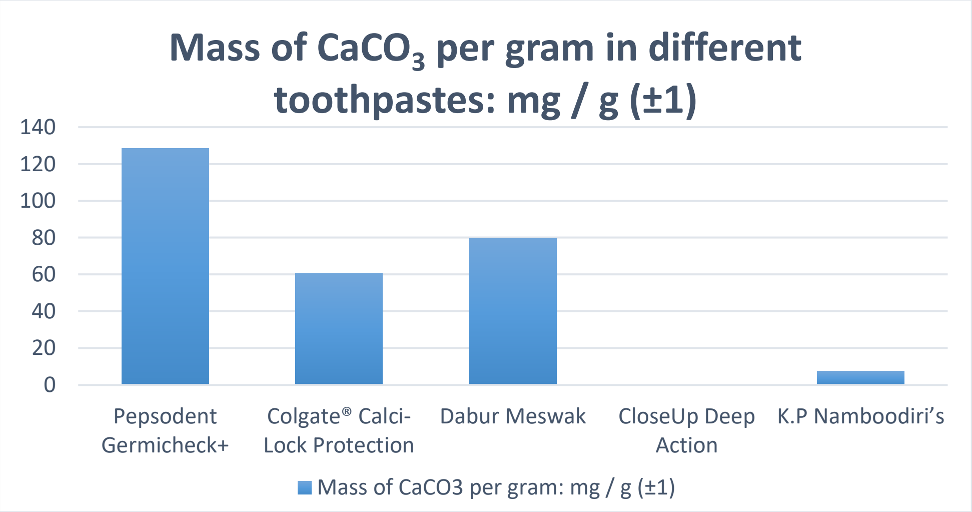
Mass of $CaCO_3$ in milligrams = No. of moles x 100.0869 x 1000

Mass of $CaCO_3$ per gram = Mass of $CaCO_3$ ÷ Mass of sample (Table 3)

Table 7: Mass of $CaCO_3$ in the different toothpastes

Toothpaste	Mass of $CaCO_3$ / mg (± 1)	Mass of $CaCO_3$ per gram: mg / g (± 1)
Pepsodent Germicheck+	134	128
Colgate® Calci-Lock Protection	62	60
Dabur Meswak	81	79
CloseUp Deep Action	0	0
K.P Namboodiri's	8	7

Figure 8: Comparison of the mass of $CaCO_3$ in the different toothpastes



10.1 Uncertainty Propagation

Uncertainty of volume of excess HCl for Pepsodent = (0.1/6.4 + 0.007/0.49 + 0.01/0.54) x 5.8 = ± 0.3 cm^3

Uncertainty of volume of HCl reacted for Pepsodent = 0.02 + 0.3 = ± 0.32 cm^3 ≈ ± 0.3 cm^3

Uncertainty of no. of moles of HCl reacted for Pepsodent = 0.0003 x 0.01 = ± (3 x 10^{-6}) mol

Uncertainty of no. of moles of $CaCO_3$ for Pepsodent = (3 x 10^{-6}) / 2 = 1.5 x 10^{-6} ≈ (2 x 10^{-6}) mol

Uncertainty of mass of $CaCO_3$ = [(2 x 10^{-6}) / 0.00134) + (0/100.0869)] x 1000 = 1.49 ≈ ± 1 mg

Uncertainty of mass of $CaCO_3$ per gram = (1/134.12 + 0.001/1.043) x 128.59 = 1.08 ≈ ± 1 mg/g

The propagation of uncertainties done for Pepsodent is given above, the value of uncertainties for other toothpastes have been propagated in the same way, and these values are shown in Table 6.

11. Analysis

From table 7, it is evident that the toothpastes Pepsodent Germicheck+, Colgate Calci-Lock Protection and Dabur Meswak have considerable amounts of calcium carbonate, with Pepsodent having the highest amount of 128 mg/g, followed by Dabur Meswak with 79 mg/g and Colgate with 60 mg/g. The other two toothpastes, CloseUp Deep Action and K.P Namboodiri's have 0 mg/g and 7 mg/g respectively, which show that there is very little or no amount of calcium carbonate in these toothpastes. From table 6, the volume of hydrochloric acid reacted shows the trend in the amount of calcium carbonate present in each toothpaste. This is because when the volume of hydrochloric acid reacted is higher, it means that more amount of acid is needed to react with all the calcium carbonate present in the toothpaste solution. For example, Pepsodent, with the most volume of hydrochloric acid reacted, 4.2 cm^3, has the highest amount of calcium carbonate, and CloseUp, with the least volume of acid reacted, 0.1 cm^3, has no amount of calcium carbonate.

12. Evaluation

The uncontrolled variable in the experiment was the colour of the toothpastes. CloseUp toothpaste was red in colour, K.P Namboodiri's toothpaste was green, and the rest of the toothpastes were white. When the toothpaste solutions were made, the CloseUp toothpaste was already having a pale pink colour, which made it difficult to observe the colour change of the phenolphthalein from colourless to pale pink, which could have resulted in systematic errors and unreliable readings. I could have used a different indicator such as Thymol blue which changes from blue to yellow, or I could have chosen other toothpastes which are white in colour. Furthermore, I could have placed the conical flask on a white tile while performing the titrations which was not included in the procedure of the experiment, so that the colour change would have been observed more accurately. It cannot be said that only calcium carbonate present in the toothpaste would have reacted with the hydrochloric acid, as other basic salts or substances in the toothpaste could have also reacted with the acid, which would result in the determined mass of calcium carbonate per gram in the toothpaste to be higher than the actual mass, which is a limitation of the experiment. Moreover, more trials could have been done for each toothpaste, and the new average could have reduced random errors in the experimental readings. Also, there may have been slight parallax errors when reading the volume of acid from the burette, contributing to systematic errors.

A positive aspect of the experiment is that the uncertainties due to the apparatus used in the experiment were minimal, and the final uncertainty of ± 1 mg / g for the mass of calcium carbonate in the toothpastes is quite small. This shows that the systematic errors in the experiment were also minimal, providing more reliability to the data collected.

13. Conclusion

From the mass of calcium carbonate per gram in the toothpastes, I have come to a conclusion that CloseUp and K.P Namboodiri's toothpastes do not contain calcium carbonate at all. The very minute amount of hydrochloric acid reacted may have been with other ingredients in the toothpastes, while there would have been actually no calcium carbonate in these toothpastes. The results obtained prove my hypothesis correct to some extent, as in my hypothesis I predicted that Pepsodent would have the highest amount of calcium carbonate because of a higher RDA value compared to other toothpastes. From the experiment, the toothpaste with the highest amount of calcium carbonate is also Pepsodent. However, in my hypothesis I had stated that CloseUp had a RDA value of 80, higher than that of Colagte (68), but from my experiment it was clear that CloseUp did not contain calcium carbonate. Therefore, the presence of abrasives other than calcium carbonate in a toothpaste, such as silica gels and aluminium oxide, contributes to its RDA value to a large extent, thus it cannot be hypothesised that toothpastes with higher amounts of calcium carbonate would also contain more amount of abrasives.

14. Bibliography

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