The Downtown Review

Volume 1 | Issue 2 | Article 2

March 2015

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Recommended Citation
Sadeghi, Ghazal; Ghaderian, Elham; and O'Connor, Anne. "Determination of Dioctyl phthalate (DEHP) concentration in polyvinyl chloride (PVC) plastic parts of toothbrushes." *The Downtown Review*. Vol. 1. Iss. 2 (2015) .
Available at: https://engagedscholarship.csuohio.edu/tdr/vol1/iss2/2

Determination of Dioctyl phthalate (DEHP) concentration in polyvinyl chloride (PVC) plastic parts of toothbrushes

Cover Page Footnote

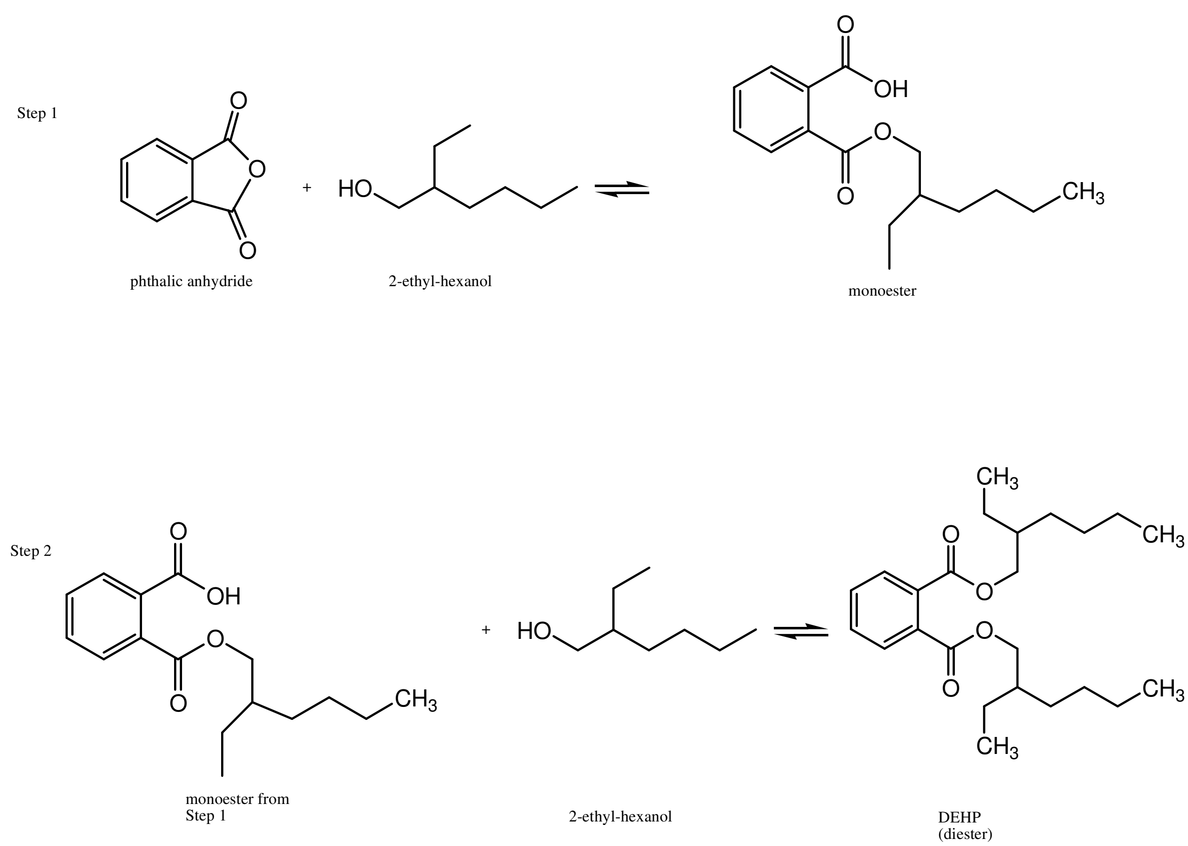
We express our thanks to Bhagya Gunasekera, Prasad, and Liann, the guides of the project for their guiding and providing all necessary facilities to carry out our project successfully.

Introduction

Phthalates are esters derived from alcohols and phallic anhydride. Their chemical structure consists of a benzene ring and two carboxylic acid groups. The most common phthalates found are Dibutylphthalate (DBP), Dimethylphthalate (DMP), and Di (2-ethylhexyl) phthalate (DEHP) (United States Environmental Protection Agency, 2012). They are chemicals that are often found in household products as well as polyvinyl chloride (PVC) plastics. Phthalates are oily, odorless, and colorless liquids that act as plasticizers to enhance the flexibility, transparency and durability of plastics (Barlow et al., 2007). According to the Environmental Protection Agency, phthalates are produced in large quantities and approximately 470 million pounds are incorporated in various products each year (EPA, 2006). Phthalates are found in various products such as liquid soap, toothbrushes, cosmetics, toys, paints, and food packaging. The magnitude, frequency, and prolonged exposure to phthalates contributes to several negative outcomes. Phthalates are often the cause of endocrine disruption, neurological damage, asthma, male reproductive system flaws, hormonal imbalances, obesity, infertility, early puberty, genital defects, premature deliveries, and testicular cancer (Barlow et al. 2007).

Currently, the FDA has announced that there is not enough evidence to support that phthalates used in cosmetics pose a safety risk. The FDA has mentioned that if a health hazard exists, they will advise the industry and the public to take action within the scope of their authority under the Federal Food, Drug, and Cosmetic Act to protect the health and welfare of consumers. This shows that more research regarding the presence of phthalates in daily products needs to be conducted. Long-term clinical research studies need to be conducted to determine the safe cutoff dose of phthalate in daily products.

Based on the daily usage of toothbrushes, this experiment mainly focuses on analyzing the amount of Dioctyl phthalate (DEHP) present in polyvinyl chloride (PVC) plastics of toothbrushes. A majority of previous studies have focused on the determination of phthalates in plastic bottled water, plastic toys, and cosmetics. However, negligible amounts of scientific experiments have been done on phthalates of toothbrushes so far. Methods mainly used in previous publications for phthalate extraction from solid and liquid materials included Solid-Phase Extraction (SPE) and Solid-Phase Microextraction (SPME) (Swedish Society for Nature Conservation 2011). For this study, though, the Gas Chromatography/Mass Spectrometry method was used, in order to identify the phthalates concentrations in the given standards and samples. The hypothesis was that the PVC plastic parts of toothbrush heads contain a significant amount of phthalates. The following diagrams represent the two steps synthesis of DEHP.



Experimental Details

Materials

Chemicals:

The chemicals used for preparing the standards of the experiment are Dioctyl phthalate (DEHP), the solute, hexane, dichloromethane, or the inert solvents. The solute DEHP has the chemical formula of $C_{24}H_{38}O_4$, and molar mass of 390.55 gr mol^{-1}. Dioctyl used in this experiment was 98% pure. Hexane with the chemical formula of $C_6H_{14}$and molar mass of 86.18 gr mol^{-1}, along with dichloromethaneCH_2Cl_2 with the molar mass of 84.93 gr mol^{-1}, were used as solvents due to their non-polar nature. Hexane and methylene chloride are also the best volatile organic compounds used for the GC/MS extraction method (Operation Procedure With Variant GC/MS). In addition to the mentioned chemicals, the other materials used to conduct the experiment were a Reach adult's toothbrush and an Equate kid's toothbrush, from which our samples came from.

Gas Chromatography/ Mass Spectrometry (GC/MS)

One of the most accurate tools for analyzing environmental samples is Gas Chromatography/Mass Spectrometry, which separates chemical mixtures (the GC part) and identifies the components at a molecular level (the MS part). Generally, the GC separates chemicals based on their volatility when the mixture is heated. One microliter of solution is injected in to the GC and heated to evaporate the chemicals into gases. There is a thin column that carries the sample via an inert gas (such as helium) through the instrument. The outer part of the GC is a special oven which heats the column to evaporate the solution. Chemicals with high volatility travel through the column more quickly than other chemicals with low volatility. The separated substances flow into the MS. Mass spectrometry identifies compounds by the mass of the analyte molecule. The data is then sent to a computer and plotted on a graph called a mass spectrum.

Procedure

For this experiment, the amount of phthalates present in toothbrushes needed to be measured. One of the general methods to determine the concentration of phthalate in the unknown toothbrush samples is to make a calibration curve. To plot the calibration curve, several standards need to be prepared using serial dilution of the stock. Serial dilution is the stepwise dilution of the known volume of stock to achieve a geometric progression of the concentration. A four-fold serial dilution would be 10 ppm, 5 ppm, 1 ppm, 0.5 ppm. Therefore, the first step was to prepare a 5 ml stock solution of 100 ppm of phthalates. The stock solution was prepared by dissolving 102 µl of DEHP in 0.05 ml of 10,000 ppm hexane. Geometric progression of this serial dilution was determined by the dilution equation:

$C_1V_1 = C_2V_2$

As an example, the first standard solution was prepared based on the following calculations:

C_2: desired concentration for standard#1 = 50 ppm V_2: desired volume for standard # 1 = 5 ml

C_1: stock=100 ppm V_1:?

100ppm X V_1 = 50 ppm X 5ml ➔ V_1= 2.5 ml of stock

All of our standards maintain a constant volume of 5 ml. Therefore, 2.5ml of the solvent was added to 2.5 ml of stock (V_1) to prepare the standard solution #1.

Standard Solutions	Desired Concentration (ppm)	Volume of Previous Solution (ml)	Volume of Solvent (ml)
5 ml of standard solution #1	50 ppm	2.5 ml of stock	2.5 ml
5 ml of standard solution #2	10 ppm	1 ml of standard # 1	4 ml
5 ml of standard solution #3	5 ppm	2.5 ml of standard # 2	2.5 ml
5 ml of standard solution #4	1 ppm	1 ml of standard # 3	4 ml
5 ml of standard solution #5	0.5 ppm	2.5 ml of standard # 4	2.5 ml

The above procedure was the same for the second solvent, dichloromethane (CH2Cl2). The preparation of the two samples – the Reach adult's toothbrush and the Equate kid's toothbrush – was done by cutting the head of each toothbrush and soaking them in both solvents for one week. Several crushes of each head were executed in order for more components of the toothbrush to enter into the solution.

As for the hazards, this experiment contains three potentially-hazardous chemical materials. Although wearing gloves was mandatory during the experiment, there was still the possibility that these chemicals would come in contact with the skin. Absorbing CH_2Cl_2 (dichloromethane) through the skin affects the central nervous system, liver, cardiovascular system, and blood. Hexane and dichloromethane cause irritation of skin, eyes and respiratory tract. They also are cancer-causing agents, though the risk level depends on the depth and duration of exposure to the chemicals. Furthermore, as mentioned in the introduction, the absorbance of DEHP has its own health risks such as neurological damage and genital problems.

Results and Discussion

The following tables illustrate the GC/MS readings of the peak areas for the standards and samples that were prepared using both solvents Hexane (table 1) and dichloromethane (table 2).

Table 1

Standards in Hexane	Concentration (ppm)	Peak area
Standard # 1	10.00	697409
Standard # 2	5.00	253955
standard # 3	2.50	105717
Standard # 4	1.00	10484
Standard # 5	0.50	6438
Sample # 1 Colgate	**1.26**	28032
Sample # 2 Colgate	**1.41**	38618
Sample # 3 Colgate	**1.02**	10127
Sample # 4 Colgate	**0.92**	2540
Sample # 5 Kids Equate	?	Not found
Sample # 6 Reach	?	Not found

Concentration and peak area readings of standards and samples in hexane

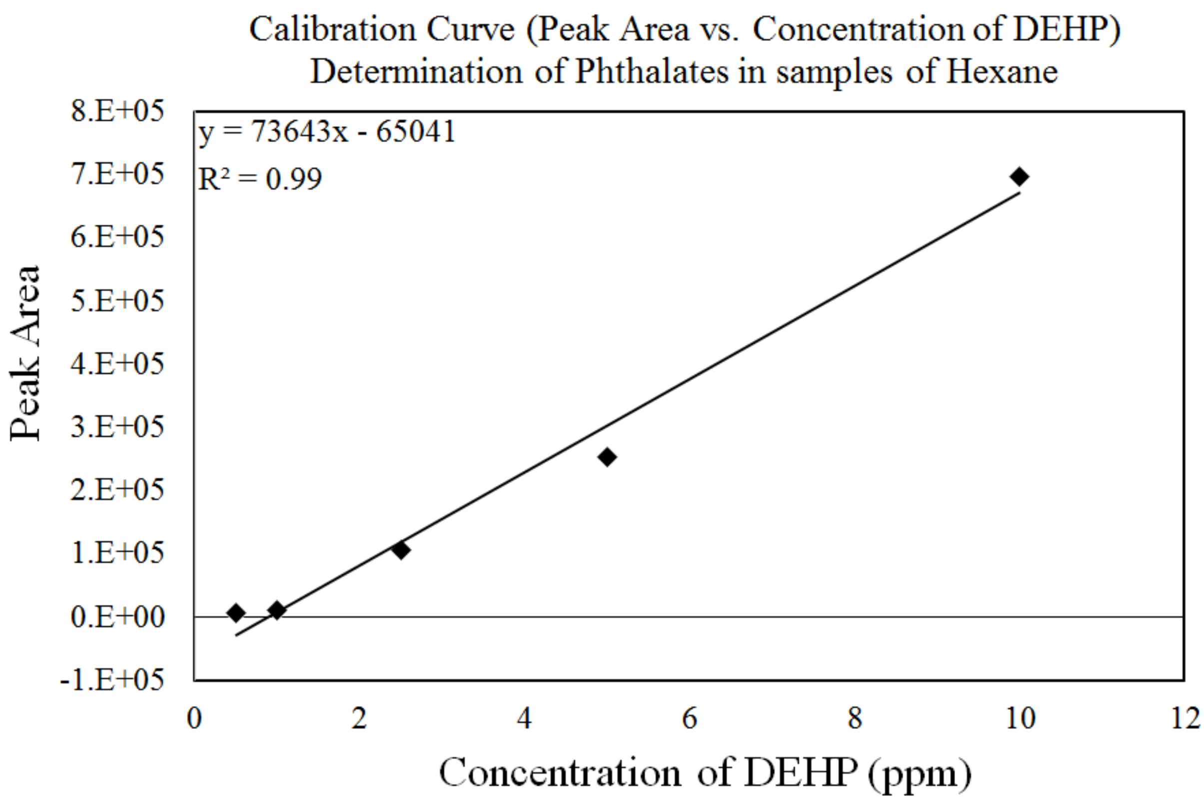
Table 2

Standards in dichloromethane	Concentration (ppm)	Peak area
Standard # 1	10.00	1.37E+06
Standard #2	5.00	2.59E+05
Standard # 3	2.50	608223
Standard # 4	1.00	357867
Standard # 5	0.50	97819
Sample # 1 Colgate	?	Not found
Sample # 2 Colgate	**1.6**	6292
Sample # 3 Colgate	?	Not found
Sample # 4 Colgate	?	Not found
Sample # 5 Kids Equate	?	Not found
Sample # 6 Reach	?	DBP

Concentration and peak area readings of Standards and samples in methyl chloride

In order to determine the phthalate concentration of the unknown samples, a calibration curve graph was plotted for each set of data.

Graph 1



Graph 1 represents the calibration curve and peak areas vs. phthalate concentration of standards that were prepared in hexane. Looking at the linear trend line equation of this graph ($y = 73643x - 65041$), x or the independent variable represents the concentration of Dioctyl phthalate present in each standard. The dependent variable y indicates the GC/MS peak area reading of each standard. Provided with this equation, phthalate concentration of the unknown sample could be calculated by taking its peak area reading and plugging that into the trend line equation to solve for x.

Sample # 1 Colgate; 28032 = 73643x - 65041→ x = 1.26 ppm

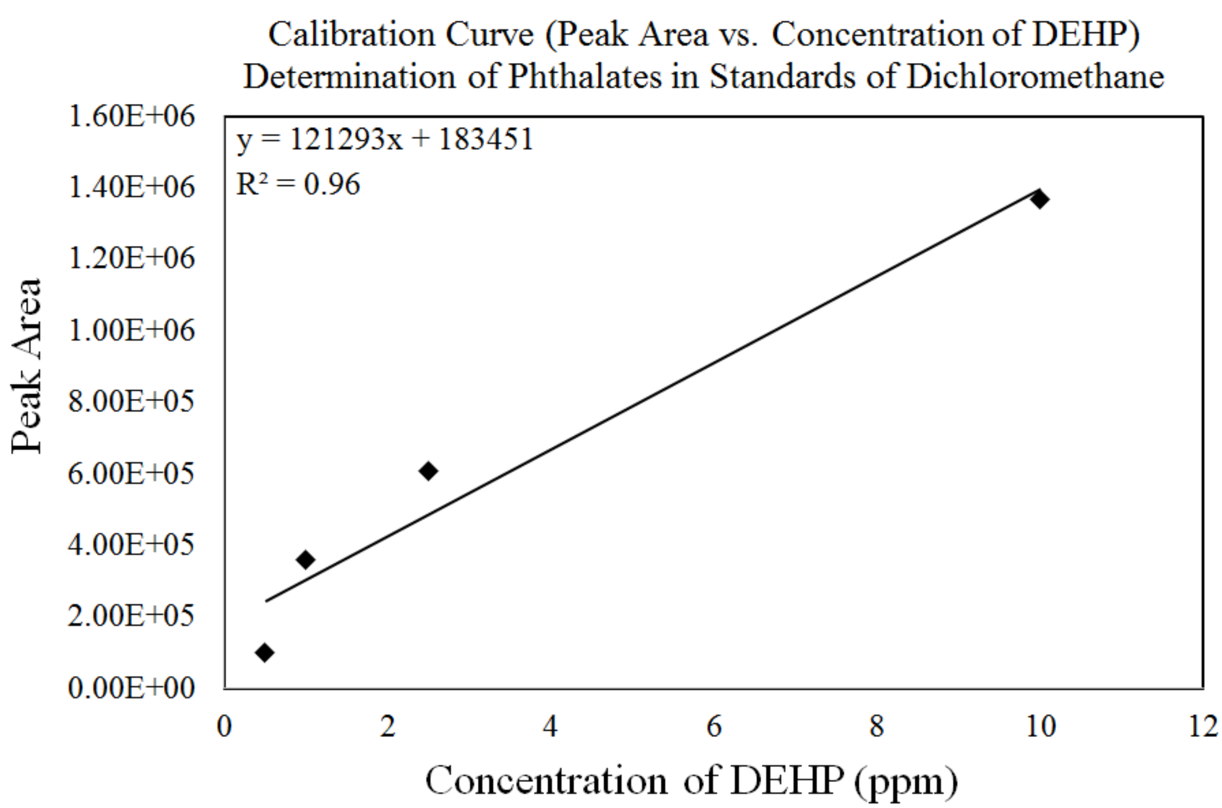
Sample # 2 Colgate; 38618 = 73643x - 65041→ x = 1.41 ppm

Sample # 3 Colgate; 10127 = 73643x - 65041→ x = 1.02 ppm

Sample # 4 Colgate; 2540 = 73643x - 65041→ x = 0.92 ppm

Therefore, all four samples of Colgate toothbrushes tested in hexane have a considerable amount of DEHP in their PVC plastic parts ranging from 1.26 ppm to 0.92 ppm. The average Diocthyl phthalate concentrations of the four Colgate samples were calculated to be 1.15 ppm. However, the Equate kid's soft power toothbrush and the Reach adult's toothbrush showed no DEHP peak area. The same calculations were carried out to determine the phthalate concentration of the sample toothbrushes in dichloromethane.

Graph 2



Graph 2 was plotted using only 4 standards because one of the standards run by the GS/MC resulted in a wrong peak area reading and therefore was affecting both the r-squared value and the equation of the trend line. The peak area for standard number 3, 2.5ppm, was expected to fall in the range of 2.5E5 to 3.59E5. The resulting peak area reading came out to be higher than what was expected: 6.1E5. As a result, the obtained r-squared value was of medium strength. Therefore, to improve both the strength of the r-squared and the accuracy of the trend line, this standard was disregarded and the above graph was derived.

To determine the phthalate concentration of four Colgate samples, the calculations previously mentioned had to be repeated. The peak area reading is plugged as y into the equation to solve for phthalate concentration x. However, only one of the samples led to a peak area reading. So the DEHP peak was not found in the other three Colgate samples. Diocthyl phthalate was not found in neither the Equate kid's power toothbrush nor the Reach adult's toothbrush:

$y = 121293x + 183451$

Sample #2 Colgate: $6292 = 121293x + 183451 \rightarrow x = 1.6$

Hence, the phthalate concentration of the Colgate sample in Dichloromethane, is equal to 1.6 ppm.

The purpose of this experiment was to determine the phthalate concentration present in the PVC plastics of toothbrushes. This study focused on the brands which did not have any phthalates listed as one of the ingredients on their labels. The average Diocthyl phthalate concentration of Colgate toothbrushes was found to be 1.15 ppm in hexane. The Equate kid's power toothbrush illustrated no presence of any phthalate concentration in both solvents. The Reach toothbrush showed existence of Dibutyl phthalate (DBP) concentration, not Dioctyl phthalate. Since the calibration curve was prepared using DEHP as a solute, the exact DBP concentration could not be found using graph 1 or 2. This study adds to the current knowledge by proving the existence of phthalate in toothbrushes; a material used daily which would certainly have negative effects on peoples' physical health across all spectrums.

Considering the results of the peak area readings of the samples from the GC/MS instrument, it is logical to conclude that hexane is a better solvent for DEHP detection compared to dichloromethane due to its inert characteristics. Hexane is a very non-polar solvent because of the small difference in electronegativity of its bonding atoms hydrogen and carbon. This is in contrast to dichloromethane, which has two very electronegative chlorine atoms contributing to its polarity. Hexane has a polarity index of 0.1 compared to dichloromethane with the polarity index of 3.1. Moreover, in this study specifically, a polar column was used in the GC/MS instrument, and thus the use of a non-polar solvent was suggested so that the polarity of solvent would not interfere with the ionization of the solute Diocthyl phthalate. In conclusion, non-polar solvents are better for phthalate detection when using a polar column in GC/MS method.

One of the solvents used in this study is methylene chloride, also called dichloromethane, which is a volatile, colorless liquid with a chloroform-like odor. Methylene chloride is used in many different industries including paint stripping, metal cleaning, and degreasing due its combustibility characteristics. Methylene chloride reacts violently with oxidizing agents, strong bases, and chemically active metals, and may corrode plastic and rubber as well. These corrosive properties of dichloromethane were observed while samples of the Reach toothbrushes were prepared. The reactions that took place between the PVC plastic parts of the toothbrush, and this solvent led to the change of color for solvent and also change of property for the PVC plastic parts of the Reach toothbrush. This interesting observation is mostly due to the redox reaction taking place between the solvent and chlorine present in the PVC parts.

Conclusion

Phthalates are chemicals found in everyday products and PVC plastics, mainly because of their ability to enhance flexibility and durability. Phthalates could have many negative effects on individuals based on their daily exposure to these materials. Toothbrushes are among those products that contain PVC plastics and are used several times a day by people all around the world. Therefore, if toothbrushes contain a significant amount of phthalate, they could be very dangerous and harmful. This experiment was done to determine the phthalate concentration of Colgate, Equate, and Reach toothbrushes. The method was Gas Chromatography/Mass Spectrometry. The results obtained showed a significant amount of phthalates in the Colgate brand toothbrushes with an average of 1.15 DEHP ppm. The phthalate present in Reach adult's toothbrush was found to be Dibuthyl, DBP. Also, for the Equate kid's power toothbrush no phthalate was found.

This experiment was a continuation of the same project started in 2013, but the previous study had a few limitations that were corrected while conducting this present research. At first, this experiment was done with the standard solutions that had the phthalate concentration of 0.5 ppm to 50 ppm. This 0.5 ppm to 50 ppm interval of phthalate concentration resulted in a calibration curve that was not a best representation of the data. The 50 ppm standard solution made the slope and y intercept of the trend line incorrectly larger, all of which resulted in a negative phthalate concentration of the Equate kid's toothbrush sample in hexane. Therefore, after statistical calculations it was concluded that 50 ppm standard solution was an outlier that needed to be removed. The current results presented in this paper are based on the smaller interval of phthalate concentration, 0.5 ppm to 10 ppm. Also, to improve the calibration curve the number of standard solutions were increased to conduct the present research while continuing the same procedures. The accuracy of the calibration curve graph is improved by increasing the number of standard solutions and as a result more accurate equation of a trend line is obtained. In this manner, the precision and accuracy of DEHP concentration reported for a specific brand was significantly improved. Another limitation of the previous study was the small number of samples taken from each brand. In this experiment, 12 samples were taken at random from the three brands of Colgate, Equate kid's, and Reach adult's toothbrush. It is critical to take at least four samples from that brand and find the average phthalate concentration present in all toothbrushes tested from that specific brand.

Further research needs to be conducted regarding the same issue with the goal of producing additional results and trying to improve the limitations of this study. In general, phthalate should be removed from the products that people use in their everyday life based on its harmful effects on human health. In return, other plasticizers should be replaced to maintain not only the flexibility and durability of products, but also to incur fewer health risks for humans and the environment.

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