Detection of Diethylene Glycol in Toothpaste

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الخلاصة:

تعد معاجين الأسنان من المنتجات دائمة الاستخدام من قبل المستهلكين لمختلف الفئات العمرية ولأغراض وقائية وعلاجية وجمالية على حد سواء لضمان صحة وسلامة الأسنان مما شجع قي حصول تنوع وتعدد كبير في إنتاجها ومعروضها السلعي، أظهرت نتائج التحري عن مادة الكلايكول ثنائي الإثلين DEG من خلال الفحوصات المختبرية ل 22 **علامة** تجارية باعتماد طريقة كروماتوغرافي الغاز GC خلو ثلاثة عينات منها والمرمزة D3 وD10 و D11، في حين أظهرت بقية العلامات التجارية احتوائها على هذه المادة السامة الملوثة وتراوح تركيزها بين 101– 839 ppm موزعا على مناشيء مختلفة فقد كانت العلامة التجارية Crest2 من ألمانيا أعلاها والعلامة التجارية Colgate2 مجهولة المنشأ أوطأها وكانت ستة عينات من المعاجين صينية الصنع تحتوي على تراكيز عالية من هذه المادة السامة رغم الشك في مصداقية المناشيء المدرجة ضمن بطاقات دلالة العينات مما يتطلب الاهتمام بفحص المعروض السلعي من قبل الأجهزة الرقابية المختصة مع موجة غش معاجين الأسنان صينية الصنع بمادة DEG.

Abstract:

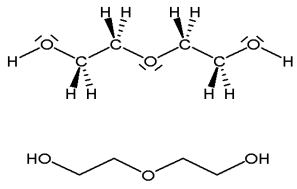
Toothpaste products are permanently used by consumers of different age groups for preventive, curative and aesthetic aspects to ensure the health and safety of the teeth. This encouraged valuable diversity in their production and commodity supply. The investigation results of DEG through laboratory tests of 22 brands showed that three samples, coded D3, D10 and D11, lacked using the gas chromatography GC technology, whereas other trademarks showed that they contain this toxic contaminants with concentration range between 101 - 839 ppm and were distributed on different origin, of which the German brand Crest2 topped the list and the unknown origin Colgate2 came at the bottom. Six Chinese-made sample pastes contain high concentrations of this toxic substance, despite doubts about the credibility of the origins included in the cards, which requires attention from competent control bodies to examine samples, especially with the current wave of fraud and the inclusion of the Chinese-made toothpaste with the DEG substance.

Introduction:

Recently, the commercial toothpaste was contaminated with the chemical materials which called Diethylene Glycol (DEG). In 1st July, 2007 The Food and Drug Administration (FDA) first warned of the presence of a Chinese-made toothpaste contaminated with a harmful species, especially in the cheap ones sold in Panama, a country that already recorded of more than 120 cases of poisoning in that same material, and later fifty people died in 2006 as a result of taking one type of treatment of cold drink that contaminated with (DEG) [1]. It was announced a total ban to import toothpaste from China and all manufacturers were demanded to provide a proof that their products free of harmful material in spite of that no registration of any cases of poisoning resulting from its use. [2,3]

The health authorities in Canada and Britain discovered the presence of DEG up to 3-4% in the types of toothpastes available in their markets imported from China. High levels of the same material in the thousands of packages of toothpaste branded (Mr. Cool) and (Excel) were also found in Panama, the Dominican Republic and Costa Rica [4]. In March 2009 there was a permanent prevention by the FDA for some types of Chinese-made toothpastes that contain more than 0.25% of that toxic substance. This prevention included sale, use and manufacture of the material listed under the list of toxic and hazardous substances to human health [5,6]. Then the World Customs Organization (WCO) warned that the spread of the contaminated toothpaste may contain industrial chemicals coming From China in some countries and alert from this kind of production of Chinese factories manufactured by proxy due to its similarity with Global brands such as toothpaste(Colgate) and other famous types which have been contaminated [7]. Then the General Authority for Food and Drug in Saudi Arabia discovered that there are seven types of toothpaste made in China containing high levels of DEG. Then followed by the FDA in toothpaste and the amount of 0.1% is available in their trade markets a trademark Best, Akura 2, Shine , Smile 2 ,Special 2 , Moon Light and Zain which have been seized all these types from the market [8].

The (DEG), also known Diglycol which is a chemical substance like a viscous liquid, Odorless, colorless with sweaty taste and has a high boiling point 245 °C and low freezing degree 10 °C, so used a contraceptive to freeze fluid in the cooling system of vehicles (Radiators) as a susceptibility to mixing with water to the possession of two of hydroxyl terminal in the composition $C4H_{10}O_3$.



Diethylene Glycol

It's used widely in industry and residential applications, it is also used in cosmetics. because it is a strong pigments solvent and also introduces in chemical industries (such as manufacturing polyester resin) and used in cement grinding industry of tobacco, glue, cork and this substance is used illegally as a substitute for glycerin by some companies because of their low price and use to improve the taste and overstraining toothpaste, because of the diversity of flavor added to the taste of peppermint or cinnamon or lemon and it can not usually add sugar for dessert, as well as the sale of those types of pastes at discounted prices [3,6].

The substance DEG is quickly absorbed by the gut to reach the blood and liver during 30-120 minute and will cause serious risk to children in general. Chronic exposure of the DEG lead to the vulnerability of the central nervous system, kidneys and liver, as in some cases lead to kidney failure and coma caused by urinating blood, The poisoning and kidney failure is the most prominent reasons that led to the death of experimental animals, the less toxic dose for human is 0.14 mg \ kg of body weight, although has a LD50 located between 1-1.63 g \ kg of body weight [9].

There is a range in human susceptibility to DEG, and the minimum dose capable of being significantly toxic is not well established. It has been suggested that 140 mg/kg (1 ml/kg of a 14% solution) is a toxic dose and ~ 1 ml/kg a typical lethal dose.

The precise toxic mechanism remains to be fully elucidated, It was initially thought it was metabolized to ethylene glycol, with the latter being the cause of acute toxicity either or oxalate formation been demonstrated, either in patients or in the laboratory. It can be metabolized via oxidation by alcohol dehydrogenase (ADH) to 2-hydroxyethoxy acetaldehyde, which is then rapidly metabolized by aldehyde dehydrogenase (ALDH) to 2-hydroxyethoxy acetic acid (HEAA) [10]. It has been suggested that HEAA and other unidentified metabolites may be the mediators of toxicity in poisoning [1]. The aims of the study examined 22 samples of different types of toothpaste that are available in the local markets of Baghdad and investigate the extent of DEG contain in these toothpaste.

Material and methods:

22 samples of different types of toothpaste available in the local markets of Baghdad were evaluated to investigate the extent of DEG contain in these toothpaste.

Diagnostic technology, gas chromatography: Gas Chromatography GC using a GC Shimatzu 2010 at the Center for Research of food contamination/ Ministry of Science and Technology for the investigation of DEG [13] after the modification procedure required in the working conditions of the device to get the best separation process of the composite guided by the so-called spiked (Spiked) and according to methods in [10,11].This method of operation of a GC

pattern is divided to improve the format of the summit and reduce the burden on the system components of the sample on the system of chromatographic Table [1],and use of a solution of 50% acetonitrile in water for washing and cleaning of the syringe to remove the remnants of samples to reduce the rate of errors, as shown:

Sample Preparation: Weight of 1gm of toothpaste and placed in a tube of centrifuge capacity of 50 ml of Polypropylene, It was added 5 ml of distilled water and mixing in vortex device for 1 minute then add 5 ml Acetonitrile to prevent the formation of foam and re-mixing for 1 minute, then centrifuging of speed 5000 g for 10 minutes, then transfer 0.5 ml of the supernatant to test tubes and added 1 ml. of Methanol (Figure-1).

Reference Standard Preparation: dilution of 0.2 ml of DEG in 5 ml Methanol and it also diluted 0.5 ml of supernatant in 1 ml Methanol.
It was used to calculate coefficient of Rt Retention by using the following equation: -

$$Cs = \frac{Cst \cdot As}{Ast}$$

Cs= Concentration of extract toothpaste sample ppm.
Cst= Concentration of standard solution DEG pmm.
As= Size of toothpaste sample mm 2.
Ast= Area of DEG standard solution mm 2

Column	SE54 (30 m Length X 0.32 mm Diameter X 0.50 µm)Thickness
Temperature Injection	240 °C
Temperature Detector	300 °C
Detector	FID
Injection Volume	1 µL
Carrier Gas Flow	at 35 cm/sec (constant flow)
Oven Program	60-150°C at (20/min),150-180°C at (10/min)

Table-1: The separation condition in Gas Chromatography GC

Statistical Analysis: The statistical program SAS (14) used to study the impact of the different factors qualities, and compared the differences between

the averages of the moral tests the least significant difference (LSD), then the correlation coefficient between some traits was calculated.

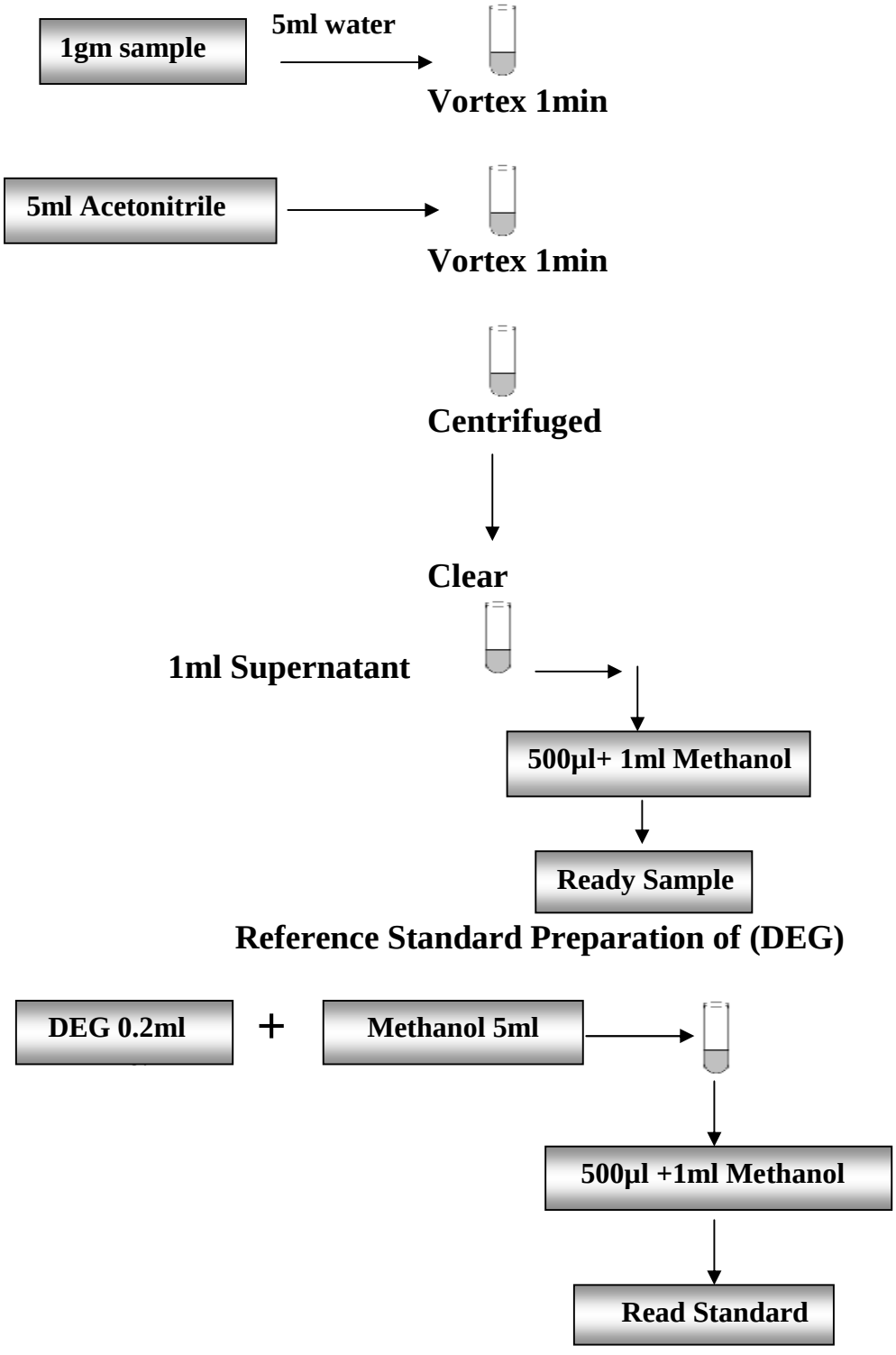


Figure-1: Preparation of Toothpaste Sample Scheme

Results and discussions:

Laboratory tests showed that samples of toothpaste encoded D3 and D10 and D11 brand Everfrest from China and Brushup and Miswak originating in the UAE, respectively, free of DEG, while consisted rest of the items set out in (Table-1) and (figure-2) of this toxic substance and a violation of the requirements of standard Iraqi authorities [9].

The varied concentrations of DEG in 19 samples of toothpaste and ranged between 101 - 839 ppm were distributed among on different origin, of which the German brand Crest2 topped the list and the unknown origin Colgate2 came at the bottom. the six toothpastes made in China contain high concentrations of this toxic substance , have doubted the credibility of the origins included in the cards denote samples of toothpaste, and this article found in the domestic sample of toothpaste brand (amber) concentration of 476 ppm which requires a full investigation by the General Company for Vegetable Oils / Ministry of Industry and Minerals (government sector) for all the substances used in the manufacture of toothpaste and make sure of their sources to the possibility of contaminated with DEG.

Statistical analysis indicated significant differences at the level of probability less than 0.05 in the concentration of DEG among samples of toothpaste made in China encoded D6, D5, D7, although the existence of this material in any concentration in the toothpaste is contrary to the requirements of the standard Iraqi numbered 1100 in 2004 on tooth paste. The study also included survey of card information for most toothpaste tubes that filled with plastic of different capacities tube, which domestically produced or imported that available in local markets of Baghdad, during the month of March 2009 (not included).

Code sample	Trade Mark	Country of origin	DEG Concentration (ppm)
D21	Crest2	Germany	839
D6	Sign	China	776
D20	Crest1	Germany	705
D5	Chuzi	China	683
D22	Aim	USA	496
D1	Amber	Iraq	476
D17	Colgate1	Saudi Arabia	320
D19	Sensodyne	-	295
D7	Sinan	China	285
D13	Signal	France	280
D15	Megadent	Bulgaria	272
D14	Formula	Indenossia	217
D2	QYZ	China	155
D8	Dentakleen	China	150
D9	Mediann	Korea	132
D4	Crust	China	126
D12	Sanino	Turkey	116
D16	Dentamint	-	112
D18	Colgate2	-	101
D3	Everfrest	China	0
D10	Brushup	United Arab Emirates	0
D11	Miswak	United Arab Emirates	0
(LSD)	---	---	* 40.733

Table-2: Estimation of Diethylene Glycol in a Gas Chromatography (GC)
***P<0.05**

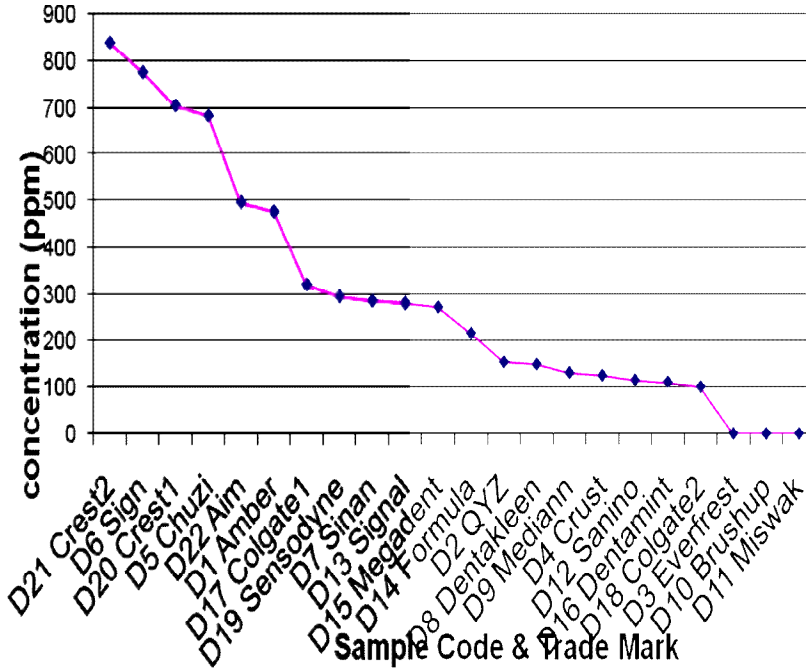


Figure-2: Diethylene Glycol in Tooth Paste

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