

Analysis of the Solid Contents of Toothpastes Available in UAE (United Arab Emirates) Markets

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Abstract

In order to find out whether any toothpastes commercially available in the United Arab Emirates (UAE) carry microplastic content in form of plastic microbeads, the filterable solid contents of 31 toothpastes from UAE markets and 2 toothpastes imported from Syria were analyzed. FT-IR studies of the solids revealed that the major solid components were hydrated silica and calcium carbonate, where the individual toothpaste product exhibited either one or the other as the dominant constituent. Titrimetric analysis of the alkalinity of the ash of the toothpastes was carried out. The solids, ashed at 600°C were subjected to FT-IR and EDS (energy dispersive X-ray spectroscopic) analysis. The ash of some of the products was shown to have TiO₂ and Ca₃(PO₄)₂ as minor components. Mostly organic dyes were used as colorants; however, iron oxide (Fe₂O₃) was also found. Importantly, none of the toothpastes carried any solid microplastic particles. Only 3 toothpastes carried microbeads at all, which were made of either silica or microcrystalline cellulose. This finding indicates that toothpastes, at least in the UAE, are no longer a significant source of microplastic in the environment. The results were compared to a toothpaste bought through the internet with a formulation from 2014, which exhibited polythene microplastic at 1.31 ± 0.39 w% of the filterable solid content.

Keywords

Toothpastes, Formulation, Microplastic, Plastic Pollution, Colorants

1. Introduction

Toothpastes contain abrasives, fluorides and detergents. Fluorides such as sodium fluoride (NaF), stannous fluoride (SnF₂), and sodium monofluorophosphate (Na₂PO₃F) have been found effective to maintain dental health [1] [2]. Detergents enable the uniform distribution of the toothpaste and improve its cleaning ability [3]. Water insoluble particles made of silica (SiO₂), calcium carbonate (CaCO₃), aluminum hydroxide [Al(OH)₃], hydroxyapatite [Ca₅(PO₄)₃OH] and calcium hydrogen phosphates, among others, constitute the abrasives that help remove the plaque from the tooth enamel [4]. It is this solid content of toothpastes that is the topic of this contribution.

In the last decades, microplastics could be found within the solid contents of certain toothpaste brands. Microplastics are plastic particles of less than 5 mm in length [5]. They have been labeled emerging environmental pollutants, reaching the aquatic environment through effluent water from wastewater treatment plants [6] [7] or directly through run-offs [8] [9], where it has been estimated that 485×10^{10} plastic particles of a size less than 5 mm are floating on the world's oceans [10]. Equally, Microplastics can be found on land, where partly they are entered into the soil through sewage sludge [11] [12]. While many microplastics, especially when made of polythene, polypropylene and polystyrene, are chemically inert and not toxic per se, additives, monomers remaining from the preparation, albeit at very low concentrations, as well as adsorbed chemicals (however also see [13]) and biological material can pose a risk to organisms, however small. While a high percentage of microplastics reaching the environment is secondary microplastic, derived from the fragmentation of meso- and microplastics, a certain fraction reaches nature as constituents of products, specifically fabricated at that small size.

Over the last 40 years, personal care products have been found to be one of the sources of such primary microplastics [14] [15]. Historically, these personal care products include rinse-off cosmetics [16] [17] [18] [19] [20] and toothpastes [21]. Microplastics have been used as abrasives as well as bulking agents in toothpastes. Sometimes, they are dyed and thus add a color pattern against a differently colored background. Nevertheless, the presence of microplastics in personal care products (PCPs) has led to many cautionary voices coming from scientists and policymakers alike [22] [23] [24] [25] [26]. Thus, in the United States of America, the US Microbead-Free Waters Act was signed into law in December 2015. The bill bans all plastic microbeads in most rinse-off cosmetic products [27], where the manufacture of microplastic containing "rinse-off" cosmetic products that have an exfoliating function was banned from July 2017, and sales were prohibited starting from July 2018 [28]. At that time, individual US states such as California and Indiana had already banned the manufacture of cosmetic products with non-biodegradable microplastics. While the USA became one of the first countries to pass a law limiting microplastic use, the ban was not all-encompassing. Microbeads that were deemed biodegradable were not

included in the ban. Nevertheless, as of July 2018, seven further countries (Canada, France, United Kingdom, New Zealand, China, South Korea, and Sweden) have established legally binding bans on microbeads through national laws or regulations. Several other countries have planned to enact such a ban, but have yet to implement legislation at the national or regional level [29]. In October 2015, Cosmetics Europe recommended its members to discontinue, by 2020, the use of synthetic, solid, plastic particles (microbeads) used for exfoliating and cleansing, that are non-biodegradable in the aquatic environment. Such new legislation limiting or downright banning microplastics in personal care products seems to have an effect on the use of microplastics in such products, even in countries that have not yet issued a ban on microplastics [20]. Currently, there are conflicting reports from different regions on the continued use of microplastics in toothpastes [14] [30] [31] [32] [33]. This led us to investigate, if toothpastes available in the United Arab Emirates, a country that does not yet have a binding ban against plastic microbeads in rinse-off cosmetics, contain microplastic or not.

2. Experimental

2.1. General

For weighing, either a Radwag balance AS 220.R2 (readability limit: 0.1 mg) or a Kern balance ABT 220-5DM (readability limit: 0.1 mg/0.01mg) was used. FT-IR spectra of the toothpastes' solid contents and their ash were measured as KBr pellets with ThermoNicolet Nexus 670 and Perkin Elmer Spectrum Two FT-IR spectrometers.

2.2. Solid Content of the Toothpastes

To 7 - 10 g of toothpaste was added 140 - 200 mL water (at exactly 1.0 g toothpaste/10.0 mL H₂O) and the resulting suspension was stirred at 50°C (WiseStir, Wisd Laboratory Instruments) until it was homogeneous. Then, it was filtered through a paper filter (Filter-Lab[®], 1300/80, pore size 43 - 48 µm). The filtrates were refiltered until they looked transparent. The filter cake was washed with water (50 mL), dried at 37°C for 14 h (Ecocell MMM, Medcenter Einrichtungen GmbH) and weighed. The experiments were carried out in triplicate. An FT-IR spectrum was taken of the respective solid. Should the solid content contain microbeads, these were separated manually from the remainder of the solid with the help of either a needle or a set of tweezers. The microbeads thus collected were analyzed and photographed under a stereoscope (model SZ2-ILST). ImageJ software was used to evaluate the microbeads for size and shape [34] [35], including the Feret's diameter. The Feret's diameter was used to represent the size of plastic particles. The Feret's diameter corresponds to the longest distance between any two points along the particle boundary [36].

The colorants except for Fe₂O₃, which could be isolated, and phthalocyanine green, the presence of which can be identified by the persistence of color under

thermolytic conditions, were directly obtained from the product labels.

2.3. Thermolysis of the Toothpastes' Solid Contents and Analysis of the Ash

500 - 900 mg samples of toothpaste solids were heated in a crucible (79C-00, Waldenwanger, Berlin) at 600°C for 2 h (Carbolite electric oven ELE 11/6), during which all adhering organic components were combusted. The thermolysis experiments were carried out in triplicate for the solid of each toothpaste. After cooling, the ash content was weighed and subjected to FT-IR spectroscopic analysis. Thereafter, the ash contents of selected toothpastes were examined with energy-dispersive-X-ray spectroscopy coupled with scanning electron microscopy (SEM-EDS) as well as with X-ray fluorescence spectroscopy (XRF). The alkalinity content of the ash was measured (as w% CaCO₃) by reacting a precisely determined amount of the ash (50 - 100 mg) with aq. HCl (0.1 M, 20 mL) at 60°C for 15 min. and subsequently back-titrating the reaction mixture with aq. NaOH (0.1 M) using phenolphthalein as indicator [37]. The titrations were carried out in triplicate.

2.4. Wavelength Dispersive XRF (WD XRF) Analysis of the Ash

Sample preparation—The ash sample obtained after thermolysis was ground to a fine powder. The resulting fine powder was pressed in a 13 mm bore steel die in a manually operated hydraulic press (Specac). The pressure was applied until the reading was stable at 10 tons and left for the 40s. This produced mechanically stable round pellets of 13 mm diameter. The pellets were generally analyzed within an hour and great care was taken that the two flat surfaces intended for XRF analysis were not touched. The weight and exact diameter of the pellet were measured and used for the semi-quantitative X-Ray analysis.

XRF Analysis—The XRF analysis was done on a wavelength dispersive (WD) XRF spectrometer (Rigaku ZSX Primus IV) equipped with an Rh X-ray tube. The instrument is controlled by ZSX Guidance software intended for the analysis of approximately 70 elements from F to U. The resulting pellet was placed in a sample holder cup with the aid of 10 µm polypropylene film which had a high X-ray transmission rate and low level of impurities. All samples were arranged on a sequential basis controlled by an automated autosampler system. The spectra were processed with a semi-quantitative SQX software package, capable of automatically correcting all matrix effects, including line overlaps. SQX also corrected for secondary excitation effect by photoelectrons (light and ultra-light elements), varying atmospheres, impurities, and different sample sizes. Finally, the spectra of each sample were matched with a library and Perfect Scan Analysis Programs [38].

2.5. Scanning Electron Microscopy (SEM)/Energy-Dispersive X-Ray Spectroscopy (EDS) Analysis

The microstructural features of the toothpaste samples were obtained using a

JEOL Analytical Scanning Electron Microscope (Model: JSM-6010PLUS/LA, Tokyo, Japan) equipped with a secondary electron imaging mode. The samples were mounted on brass stubs using double-sided adhesive carbon tape as a conductor path and were sputter-coated with gold up to 15 nm thickness using a Cressington 108 auto sputter coater and thickness controller MTM-20. Fields of the sample were inspected under a high-vacuum (ULVAC KIKO Inc, Model: G-100DB, Miyazaki, Japan) and micrographs of the sample were recorded using InTouch Scope JSM software using a power of 20 kV. The elemental composition was examined by JEOL-SEM equipped with an energy dispersive X-ray detector (EDS).

2.6. Floating Experiments with the Solid Contents of the Toothpastes—Analysis of Floating Microplastics (MPs)

Most microplastics, especially those consisting of polythene, have a lower density than water, *i.e.*, less than 1.0 g/mL. Following the method of Ustabasi and Baysal [30], the filtered and dried solids of the respective toothpastes were stirred rapidly in water (1.0 g solid/100 mL H₂O) at rt for 5 min. Then, the solids were allowed to settle for 2 h. Thereafter, the surface of the water was inspected visually for any floating solids. Any floating solids were skimmed off with a spatula spoon and refloated in deionized water (150 mL) in a separate beaker to remove any water-soluble material and any adhering particles. The refloated particles were transferred to a weighing paper and dried at 37°C for 10 h (Ecocell MMM, Medcenter Einrichtungen GmbH). Thereafter, the solids were weighed [Kern balance ABT 220-5DM (readability limit: 0.1 mg/0.01mg)], studied under a stereoscope (model SZ2-ILST) in regard to their apparent morphology and their size, and submitted to FT-IR spectroscopy (Perkin Elmer Spectrum Two). In case of an observed presence of microplastic, the material was subjected to DSC (differential scanning calorimetry) analysis (see below).

2.7. Differential Scanning Calorimeter (DSC)

The thermal response of the isolated microplastic from toothpaste (H-1) was measured using a differential scanning calorimeter (Shimadzu DSC-60 Plus, Japan). About 7 mg of powdered sample was precisely weighed into a DSC sample pan, which was sealed with a top lid utilizing a pellet press. The sample was measured in the temperature range of 25°C - 300°C at a heating rate of 10°C/min under a constant flow of N₂ (50mL/min). Data analysis was performed using the LabSolutions TA software [39].

3. Results and Discussion

3.1. Ash Content of the Toothpastes

The examined toothpastes exhibited a solid content of 11.18 ± 0.12 w% to 48.55 ± 0.28 w%, as shown in **Table 1**. Previously collected data shows this to be in the normal range of abrasive content (8 w% - 50 w%) in toothpastes [40] [41]. As

Table 1. Ash content of the sampled toothpastes.

Toothpaste	Solid content w% ± SD	Ash content w% ± SD	Main abrasive material	Alkalinity of ash expressed in w% equiv. CaCO ₃	Floating experiment
T1	15.53 ± 1.87	85.13 ± 0.72	Silica	0.65 ± 0.50	(-)
T2	13.67 ± 0.07	90.99 ± 1.18	Silica	0.88 ± 0.06	(-)
T3	43.35 ± 1.33	91.33 ± 0.25	CaCO ₃	quant. (104.0 ± 0.0)	(-)
T4	20.20 ± 1.30	87.27 ± 1.07	Silica	0.86 ± 0.17	(-)
T5	40.31 ± 0.23	97.26 ± 0.56	CaCO ₃	quant. (100.1 ± 0.0)	(-)
T6	22.63 ± 0.42	88.73 ± 2.20	Silica	- (no alkalinity)	(-)
T7	23.81 ± 0.52	88.60 ± 3.72	Silica	1.13 ± 0.48	(-/+)
T8	16.38 ± 1.12	82.31 ± 0.97	Silica	0.95 ± 0.03(5)	(-)
T9	18.52 ± 1.04	91.85 ± 2.61	Silica	1.25 ± 0.95	(-)
T10	38.83 ± 3.02	96.04 ± 0.76	CaCO ₃	quant. (105 ± 0.5)	(-)
T11	15.25 ± 0.39	90.10 ± 1.87	Silica		(-)
T12	18.93 ± 0.47	87.43 ± 3.67	Silica	1.08 ± 0.38	(-)
T13	40.13 ± 1.07	93.93 ± 1.14	CaCO ₃ and others	quant. (100.2 ± 0.1)	(-/+)
T14	40.71 ± 0.33	98.39 ± 0.53	CaCO ₃	quant. (107.89 ± 0.12)	(-)
T15	48.55 ± 0.28	93.68 ± 0.64	CaCO ₃	quant. (100.4 ± 1.4)	(+)
T16	39.64 ± 0.90	69.50 ± 0.95	Alumina/aluminum hydroxide	0.61 ± 0.26	(-)
T17	36.67 ± 1.44	90.91 ± 2.29	CaCO ₃	94.85 ± 3.20	(-)
T18	39.69 ± 2.20	95.06 ± 0.56	CaCO ₃	quant. (106.4 ± 0.8)	(+)
T19	20.35 ± 2.54	80.54 ± 3.92	Silica	1.41 ± 0.59	(-)
T20	17.12 ± 0.56	87.51 ± 2.14	Silica, mica	0.92 ± 0.34	(-)
T21	43.35 ± 0.58	95.38 ± 0.77	CaCO ₃	68.20 ± 5.90	(-)
T22	14.25 ± 0.31	84.79 ± 2.14	Silica	- (no alkalinity)	(+)
T23	15.67 ± 0.19	78.26 ± 3.17	Silica	- (no alkalinity)	(-)
T24	37.97 ± 0.30	95.42 ± 0.73	CaCO ₃	quant. (100.26 ± 0.12)	(-)
T25	41.33 ± 2.19	97.63 ± 0.29	CaCO ₃	98.30 ± 1.05	(-)
T26	24.29 ± 1.55	79.20 ± 6.58	Silica	- (no alkalinity)	
T27	11.18 ± 0.12	76.41 ± 0.85	Silica and alumina	- (no alkalinity)	(-)
T28	16.73 ± 1.05	85.96 ± 4.66	Silica	- (no alkalinity)	(-)
T29	18.5 ± 1.31	74.85 ± 0.74	Silica	- (no alkalinity)	(-)
T30	16.85 ± 0.28	82.66 ± 2.41	Silica	- (no alkalinity)	(-)
T31	16.99 ± 0.84	79.07 ± 4.63	Silica and others	5.3 ± 2.3	(-)
S1	27.0 ± 1.16	95.0 ± 0.96	Silica and CaCO ₃	91.1 ± 0.2	(-)
S2	16.18 ± 0.54	84.43 ± 2.24	Silica	0.86 ± 0.08	(-)
H1	20.34 ± 0.59	83.31 ± 0.60	Silica and PE MP	0.95 ± 0.01	(+)

major abrasive components, the toothpastes for the most part had either silica or calcium carbonate, whereas toothpaste brands typically offered at least one toothpaste of each version. Those toothpastes with silica as the major ingredient have little alkalinity. **Table 1** shows the alkalinity values obtained through titration expressed in w% CaCO₃. Numbers of CaCO₃ exceeding 100 w% of the ash, as found in T3, T10, T13-T14, and T18 indicate that these toothpastes have in addition to CaCO₃ other basic salts.

Also, the ash content of selected toothpastes was used the determination of the elemental composition of the solids using the WD XRF analysis method. All the results are expressed in mass% and calculated based on the weight of ash obtained after pyrolysis. The multi-element analysis report for each sample is shown in **Table 2**.

Table 2. Multielement X-ray fluorescence analysis report.

No.*	Component	Result (mass%)	Element line	Peak Intensity (Kcps)
T1	Si	100	Si-K α	2.841
T2	Si, Zn	99.0, 1.0	Si-K α , Zn-K α	2.821, 0.22
T3	Mg, Al, Si, S, Ca, Sr	0.45, 0.13, 5.80, 0.41, 93.0, 0.10	Mg-K α , Al-K α , Si-K α , S-K α , Ca-K α , Sr-K α	0.095, 0.089, 5.801, 0.956, 78.085, 1.104
T4	Al, Si, P, S, Ca, Fe	0.12, 98.10, 0.14, 0.66, 0.86, 0.08	Al-K α , Si-K α , P-K α , S-K α , Ca-K α , Fe-K α	0.091, 64.877, 0.067, 0.311, 0.242, 0.091
T10	Mg, Al, Si, S, Ca, Ti, Sr	0.37, 0.14, 7.55, 0.34, 89.1, 2.39, 0.04	Mg-K α , Al-K α , Si-K α , S-K α , Ca-K α , Ti-K α , Sr-K α	0.082, 0.105, 7.309, 0.801, 76.104, 0.209, 0.487
T11	Si	100	Si-K α	2.881
T12	Si, Zn	99.10, 0.86	Si-K α , Zn-K α	2.817, 0.187
T15	Mg, Al, Si, S, K, Ca, Sr	0.75, 0.32, 4.92, 0.64, 0.14, 93.0, 0.12	Mg-K α , Al-K α , Si-K α , S-K α , K-K α , Ca-K α , Sr-K α	0.157, 0.217, 4.536, 1.499, 0.168, 76.993, 1.437
T16	Al, Si	96.2, 3.82	Al-K α , Si-K α	2.99, 0.03
T17	Si, S, Ca, Sr	4.40, 0.37, 95.1, 0.15	Si-K α , S-K α , Ca-K α , Sr-K α	4.400, 0.368, 95.086, 0.149
T20	Na, Al, Si, S, Ca, Fe, Zn	0.32, 0.41, 96.50, 1.15, 0.75, 0.12, 0.76	Na-K α , Al-K α , Si-K α , S-K α , Ca-K α , Fe-K α , Zn-K α	0.023, 0.293, 62.162, 0.019, 0.552, 0.214, 0.137, 3.54
T21	Mg, Al, Si, S, Ca, Fe, Sr	0.90, 0.11, 5.10, 0.24, 93.41, 0.12, 0.06	Mg-K α , Al-K α , Si-K α , S-K α , Ca-K α , Fe-K α , Sr-K α	0.896, 0.104, 5.10, 0.241, 93.422, 0.114, 0.058
T23	Si	100	Si-K α	2.998
T26	Na, Mg, Al, Si, P, S, K, Ca, Fe, Si	0.50, 0.61, 0.15, 8.94, 0.32, 0.25, 89.0, 0.12, 0.06	Na-K α , Mg-K α , Al-K α , Si-K α , P-K α , S-K α , K-K α , Ca-K α , Fe-K α , Sr-K α	0.535, 0.798, 0.220, 14.564, 0.538, 0.096, 0.217, 82.622, 0.099, 0.037
T27	Na, Al, Si, S, K, Ca, Ti, Fe	0.36, 37.4, 59.7, 0.17, 0.42, 0.41, 1.54, 0.06	Na-K α , Al-K α , Si-K α , S-K α , K-K α , Ca-K α , Ti-K α , Fe-K α	0.405, 43.879, 54.409, 0.138, 0.162, 0.181, 0.801, 0.026
T28	Na, Al, Si, S, Cl, K, Ca, Ti, Zn	0.49, 0.24, 93.40, 0.81, 0.15, 0.22, 0.39, 3.52, 0.82	Na-K α , Al-K α , Si-K α , S-K α , C-K α , K-K α , Ca-K α , Ti-K α , Zn-K α	0.025, 0.150, 54.823, 0.365, 0.018, 0.048, 0.105, 0.391, 3.371
H1	Na, Al, Si, P, S, K, Ca, Fe	1.23, 0.51, 96.4, 0.24, 0.36, 0.55, 0.26, 0.22	Na-K α , Al-K α , Si-K α , P-K α , S-K α , K-K α , Ca-K α , Fe-K α	0.066, 0.384, 65.541, 0.126, 0.186, 0.137, 0.080, 0.272
S2	Al, Si, S	26.6, 71.7, 1.66	Al-K α , Si-K α , S-K α	0.747, 1.216, 0.034

*The numbers of selected ash content of toothpaste.

As mentioned above, most of the samples contain silica and calcium carbonate/calcium hydrogen phosphate as major components, even though samples T16 and T27 carry alumina/aluminum hydroxide as the major component. All of these compounds mainly act as abrasives and are usually used as major components in formulations of toothpastes [42]. The presence of calcium, silica and alumina is identified and quantified by characteristic elemental spectra of each element (calcium, silicon, and aluminum) as presented in **Figure 1**. The spectrum for each element is the same for each toothpaste. Solely, the intensity varies (expressed in Kcps as shown in **Table 2**) based on the concentration of the element. A small peak of the K α satellite is characteristic of silica and alumina.

The other minor elements in the ash observed were titanium, strontium, iron, zinc, magnesium, potassium, phosphorus, and sulfur. The X-fluorescence spectra for magnesium, sulfur, phosphorous, potassium and sodium are presented in **Figure 2** (taken from sample T26), the spectra for strontium and iron are presented in **Figure 3** (for sample T26) and the spectra for zinc and titanium are presented in **Figure 4** (for sample T28). Titanium dioxide (TiO₂) is used as an opacifying agent in toothpastes and was found in T10, T27 and T28 in quantities of <5.0 w%. The European Chemicals Agency (Echa) considers that TiO₂ may cause cancer if inhaled. In 2022, the EU classified the substance as a suspected carcinogen by inhalation in certain powder forms. Thus, titanium dioxide (as E171) is no longer considered safe, when used as a food additive [43].

Also, ash samples of selected toothpastes were analyzed with energy-dispersive-X-ray spectroscopy coupled with scanning electron microscopy (SEM-EDS) (**Figure 5** and **Figure 6**). As expected silicon and calcium were found to be the most abundant elements, attributable to SiO₂ and CaCO₃. Mg is attributed to CaMg(CO₃)₂ or MgCO₃, Ti to TiO₂, Fe mostly to Fe₂O₃. P we believe to be attributed to Ca₃(PO₄)₂ as sodium monofluorophosphate (Na₂PO₃F) is water-soluble.

3.2. Microbeads, Floating Experiments and the Quest to Find Microplastics as Constituents

Floating experiments were conducted with all 34 toothpastes (**Table 1**). Only

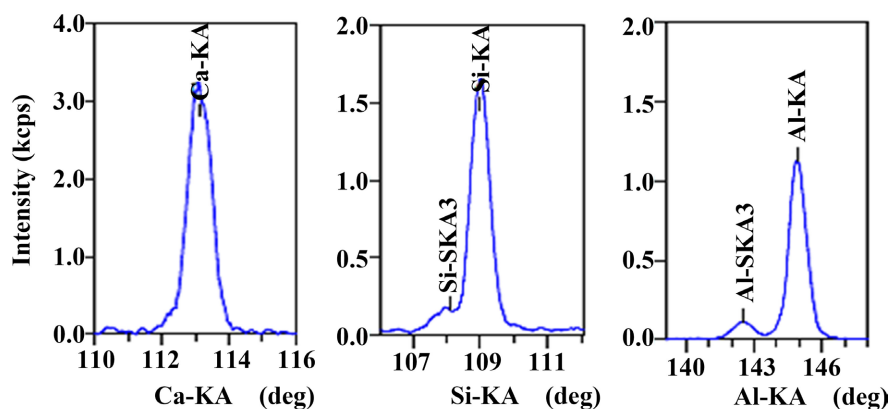


Figure 1. X-ray fluorescence spectra intensity versus 2θ functions of K α rays of Ca, Si and Al (the major components of the ash sample T26).

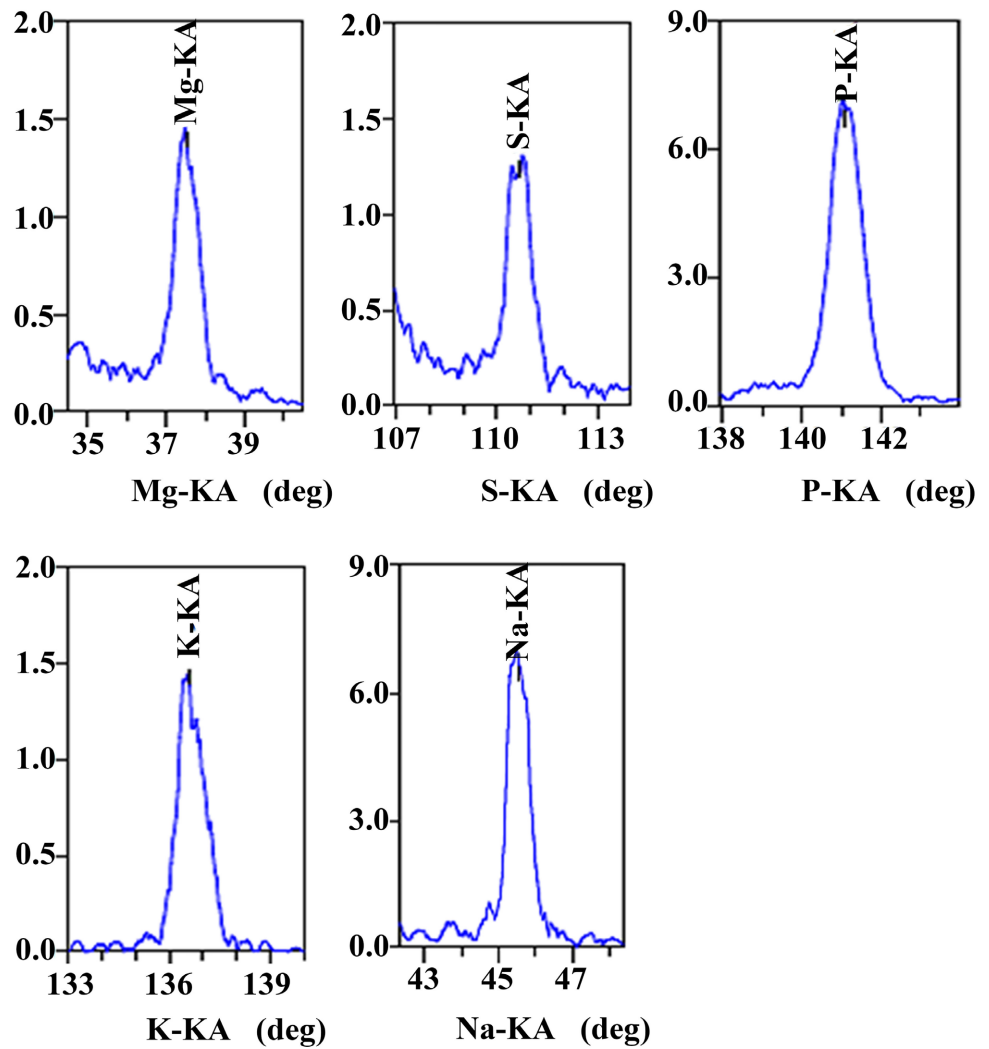


Figure 2. X-ray fluorescence spectra intensity versus 2θ functions of $K\alpha$ rays of Mg, S, P, K and Na (ash sample T26).

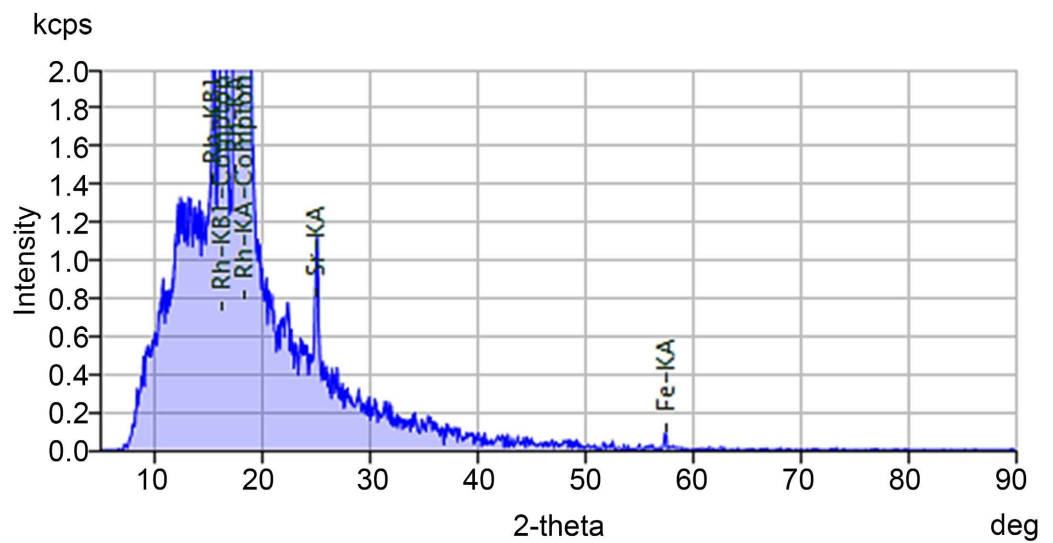


Figure 3. X-ray fluorescence spectra of Sr and Fe (ash sample T26).

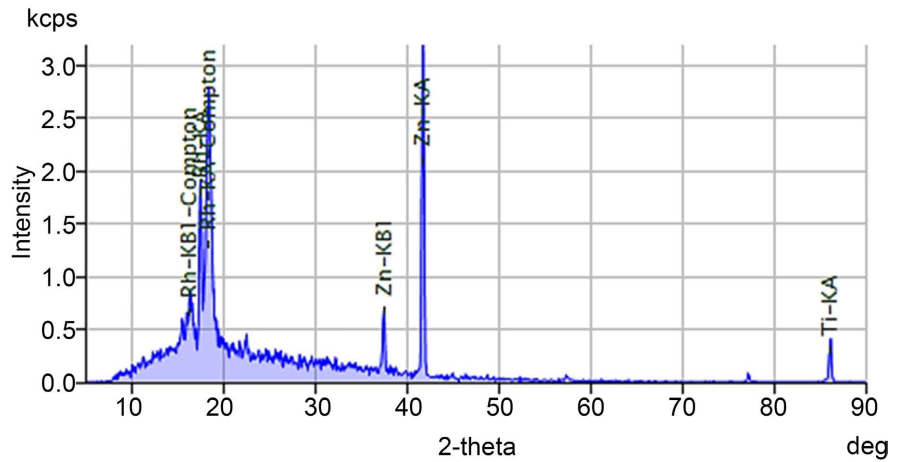


Figure 4. X-ray fluorescence spectra of Zn and Ti (ash sample T28).

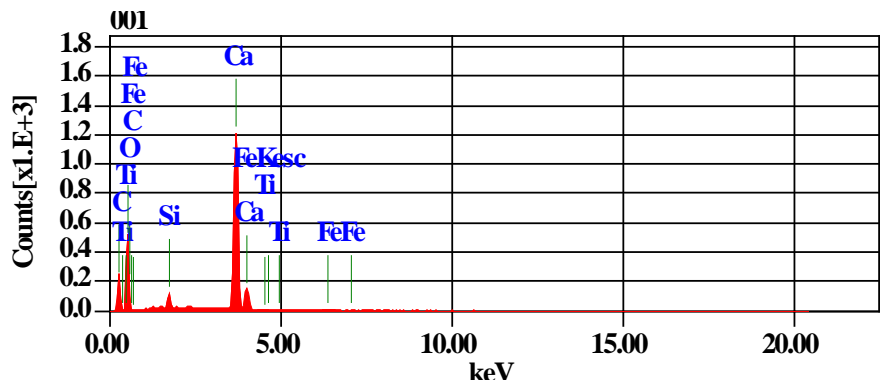


Figure 5. Energy dispersive X-ray spectrum (EDS) of the ash sample T15. C 17.61 mass% 26.86 atom%; Si 1.76 mass% 1.15 atom%; Ca 29.44 mass% 13.45 atom%; Fe 0.04 mass%; 0.01 atom%; Tind.

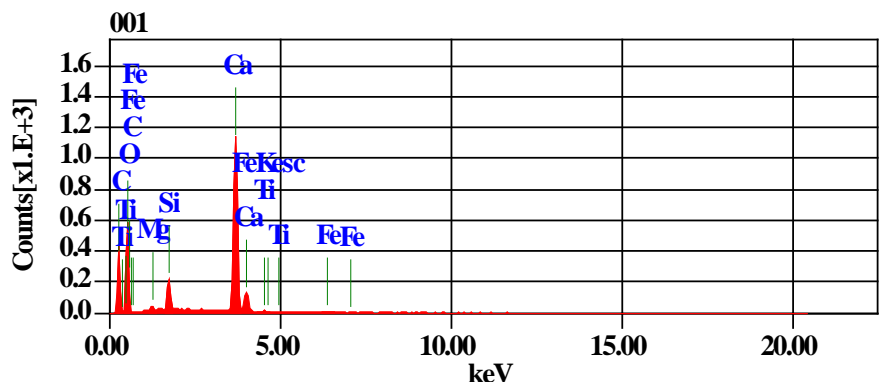


Figure 6. Energy dispersive X-ray spectrum (EDS) of the ash sample T10. C 26.07 mass% 37.18 atom%; Si 2.66 mass% 1.62 atom%; Ca 23.16 mass% 9.90 atom%; Mg 0.54 mass% 0.38 atom%; Ti 0.01 mass%; Fend.

four toothpastes (T15, T18, T22, and H1) exhibited solid content when floated on the water. Two others (T7 and T13) had floating solid content that settled after several hours. The floating material of T15, T18, and T22 was filtered off and analyzed by IR spectroscopy to be inorganic components such as mica and small

crystallites of CaCO_3 . Only three toothpastes (T5, T8, and T11) bought in UAE markets and the toothpaste (H1) purchased online were found to have microbeads. They could be isolated by direct filtration of the aqueous mixture of the toothpaste and subsequent manual separation (see 2.2., above). Of these, T5 was found to have red and blue beads, composed of silica and microcrystalline cellulose, respectively, T8 possessed blue-green beads made of silica and T11 blue beads, again made of silica. These microbeads were studied under the stereoscope. The micrographs were evaluated to determine the size distribution of the beads. Typically, for T8 the sizes of the microbeads were in the range of 20 - 70 μm (**Figure 7**).

Only H1 was found to have plastic beads, namely green and white microparticles made from polythene. Polythene was unequivocally identified by IR spectroscopy—2919 (CH_2 asymmetric stretching vibration), 2851 (CH_2 symmetric stretching), 1473 and 1463 (bending deformation), 1366 and 1351 (wagging deformation), 1306 (twisting deformation), 1176 (wagging deformation), and 731 - 720 cm^{-1} (rocking deformation) [44]. Also, differential scanning calorimetry (DSC, **Figure 8**) with a peak at 125 °C showed the typical thermal behavior of polythene [45]. The polythene microbeads made up 1.31 ± 0.39 w% of the filterable solid content of H1.

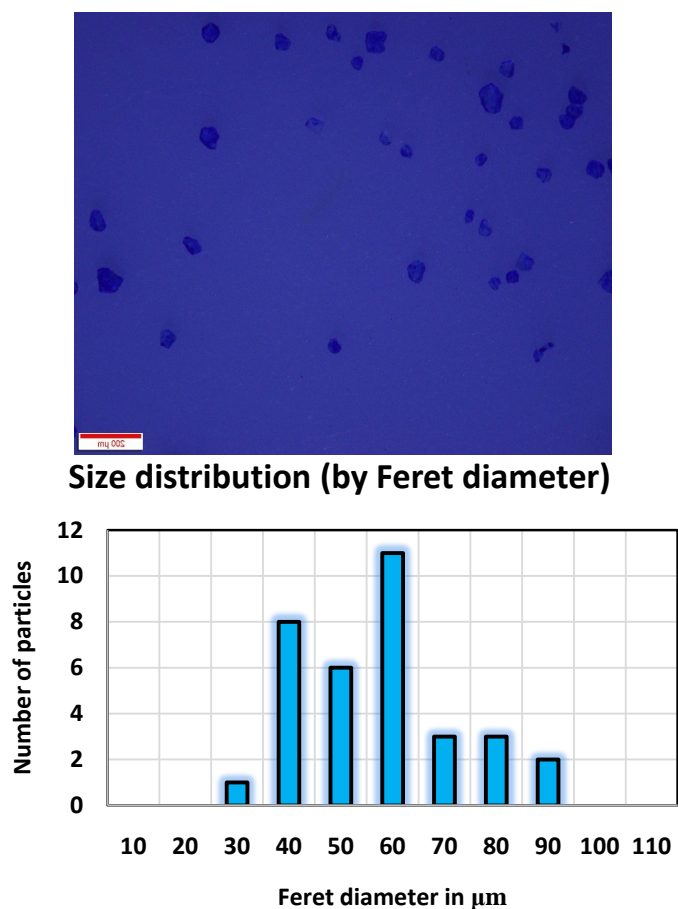


Figure 7. Micrograph of beads of product sample T8 with size distribution.

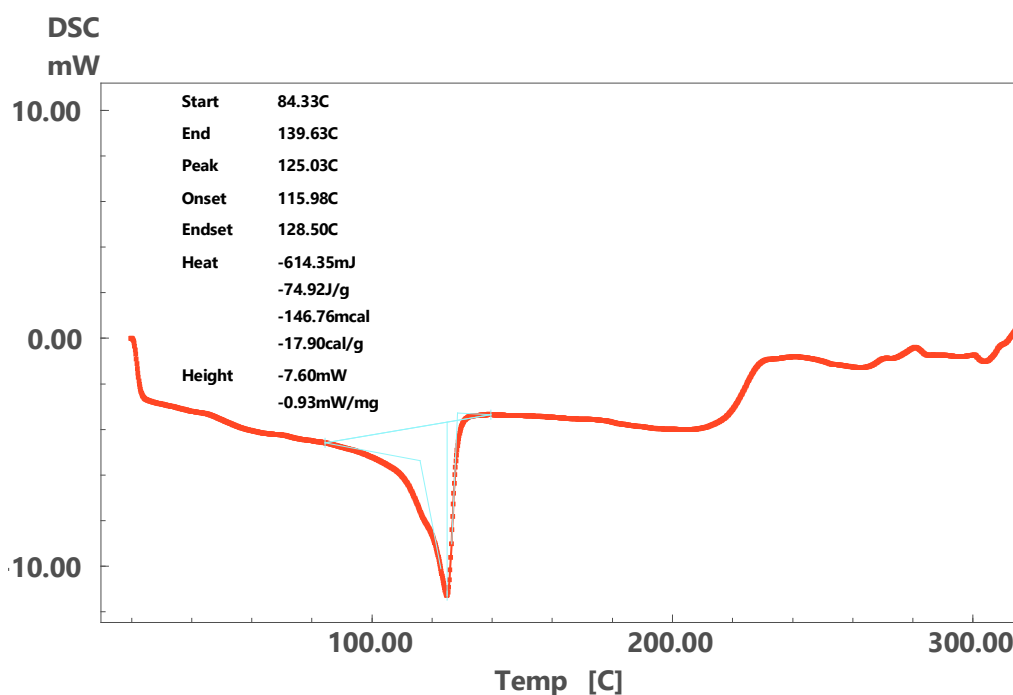


Figure 8. DSC thermogram of the microbeads of product H1.

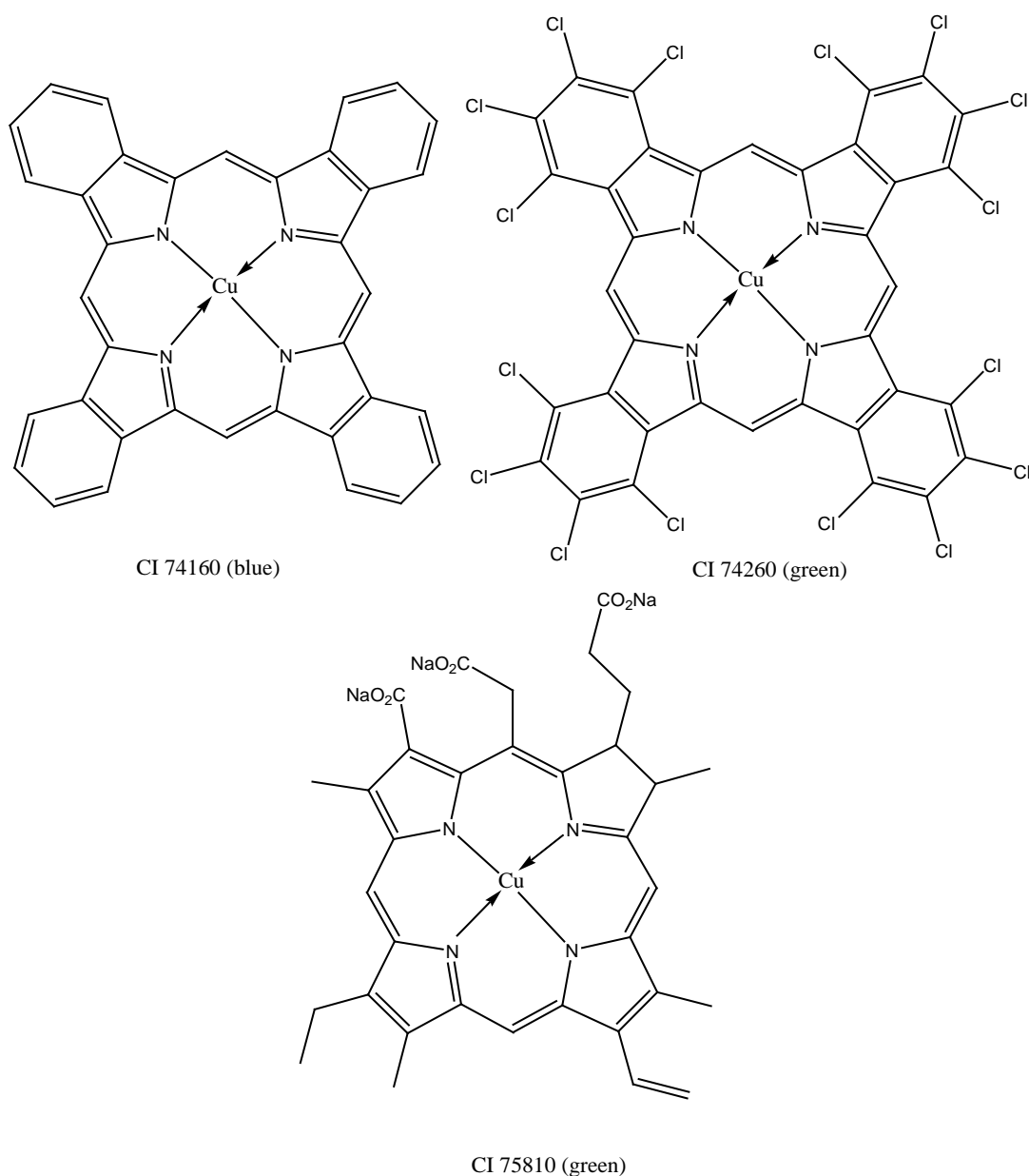
The indication that microplastic containing toothpastes are no longer available directly from UAE markets contrasts with recent studies from Turkey [30] and India [33] that seem to suggest that microplastic containing toothpastes can still be bought in these countries. Also in China microplastics have still been found in toothpastes [46]. Nevertheless, the current study is an indicator that the ban on microplastic content in rinse-off cosmetics, including toothpastes, in an ever increasing number of countries has a beneficial effect also on products that are sold in regions where bans have not yet taken hold.

3.3. Colorants

21 out of the 31 toothpastes (67.7%) bought in UAE markets were significantly colored (Figure 9). 10 out of the 31 toothpastes (32.3%) contained titanium dioxide (TiO₂) as a white pigment. As colors green (11 toothpastes, 35.5%) and blue (7 toothpastes, 22.6%) optically featured the most often. While clearly not all toothpastes list dye or pigment contents, phthalocyanine green (CI 72460, 4 toothpastes, 12.9%), chlorophylline (CI 75810, 1 toothpaste, 3.2%), and fast green FCF (CI 42053, 1 toothpaste, 3.2%) are green colorants used, brilliant blue FCF (E 133, CI 42090, also known as blue lake 1, 5 toothpastes, 16.1%), phthalocyanine blue (pigment blue, CI 74160, 4 toothpastes, 12.9%), and acid blue (CI 42051, 1 toothpaste, 3.2%) are the blue colorants used. Brilliant blue FCF (E 133) has been banned as a food colorant in several European countries, including France and Germany. Iron oxide (CI 77491, 4 toothpastes, 12.9%) and CI 12490 (pigment red 5, N-(5-chloro-2,4-dimethoxyphenyl)-4-[[5-[(diethylamino)sulphonyl]-2-methoxyphenyl]azo]-3-hydroxynaphthalene-2-carboxamide, 2 toothpastes, 6.5%)

are used as red ochre and bright-red colorants, respectively. Finally, tartarazine (E 102, CI 19140, 3 toothpastes, 9.7%), quinoline yellow (quinoline WS, CI 47005, 1 toothpaste, 3.2%), and yellow iron oxide (CI 77492, 1 toothpaste, 3.2%) represent the yellow colorants used. Tartarazine (E 102) is banned as a food colorant in Norway and Austria.

The two Syrian bought toothpastes carried TiO_2 (for S1) and quinoline yellow WS (E104, CI 47005) and brilliant blue CFC (for S2, E133, CI 42090). Finally, also the toothpaste that was bought online, having an expiry date of 2016, used brilliant blue FCF (E133, CI 42090) and quinoline yellow WS (E104, CI 47005). Quinoline is deemed not to present any health risk, and is even permitted as a colorant in beverages in the European Community and in Australia. The toothpaste also included iron oxide.



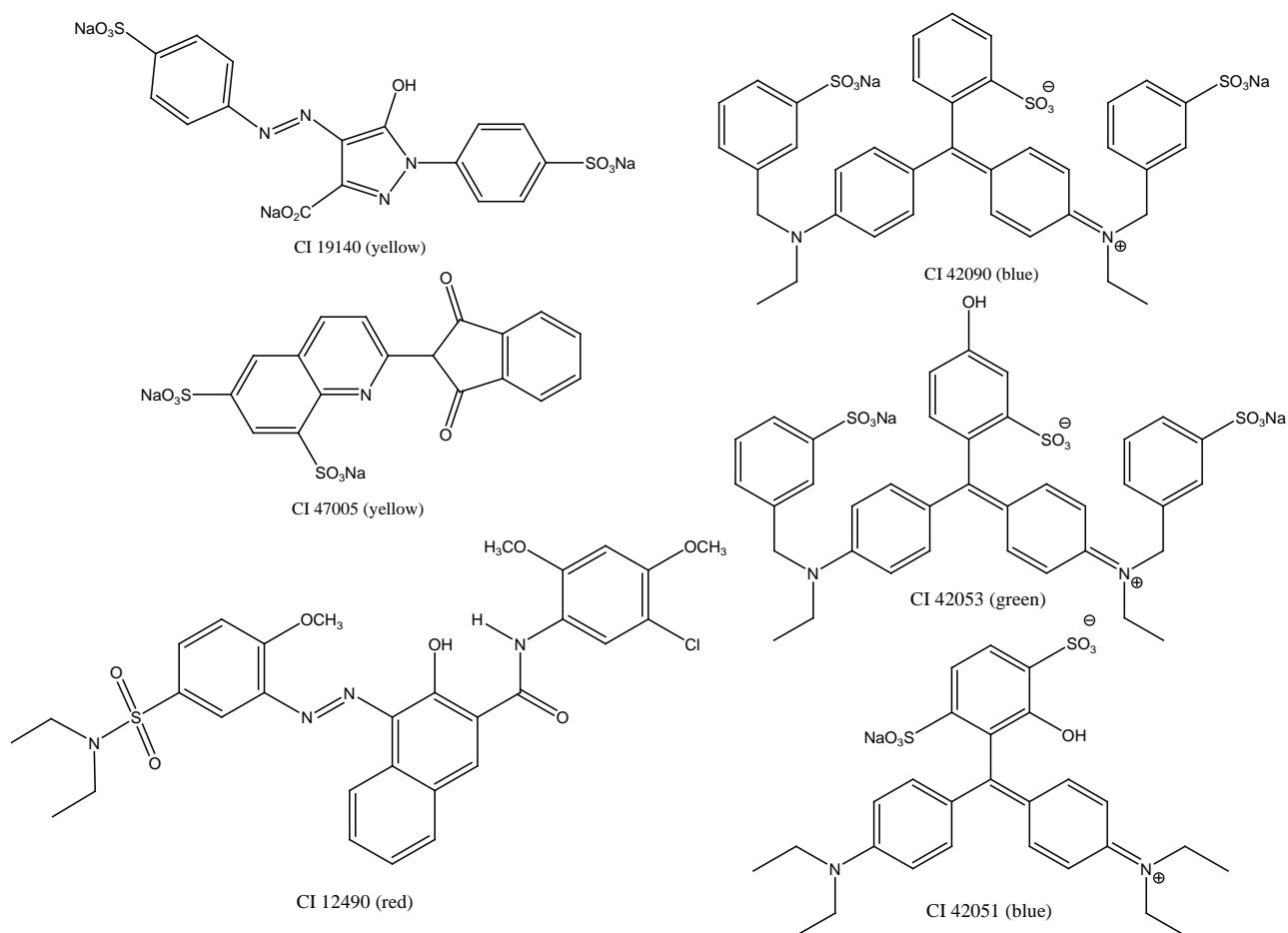


Figure 9. Colorants found in the analyzed toothpastes.

4. Conclusion

The solid contents of 31 toothpastes from across the main brands, bought in UAE markets, and of 2 toothpastes synthesized and acquired in Syria were studied. None of the toothpastes showed microplastic content. This is a good indication that microplastic content in toothpastes in these countries is being/has been phased out. Therefore, it seems that restrictive regulations in countries of the European Community, the United States and other countries in regard to microplastic in rinse-off cosmetics have a beneficial effect of reducing microplastic containing personal care products also in other regions. By chance, for this study, toothpaste could be acquired online that, long past its expiry date, included polythene based microplastic in its formulation. It is important to note that when toothpastes are formulated with microplastic content, then microplastic is an abundant constituent in the products that cannot be overlooked and should not be seen and analyzed as a sparse contaminant.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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