



Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: [www.elsevier.com/locate/chroma](http://www.elsevier.com/locate/chroma)



# Pressurized liquid extraction–gas chromatography–mass spectrometry for confirming the photo-induced generation of dioxin-like derivatives and other cosmetic preservative photoproducts on artificial skin<sup>☆</sup>

Gerardo Alvarez-Rivera<sup>\*</sup>, Maria Llompart, Carmen Garcia-Jares, Marta Lores

Department of Analytical Chemistry, Nutrition and Food Science, Faculty of Chemistry, Campus Vida, University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain

## ARTICLE INFO

### Article history:

Received 6 December 2015  
Received in revised form 19 February 2016  
Accepted 22 February 2016  
Available online xxx

### Keywords:

Personal care products  
Preservatives  
Photodegradation  
Pressurized liquid extraction  
GC–MS  
2,8-Dichlorodibenzo-*p*-dioxin

## ABSTRACT

The stability and photochemical transformations of cosmetic preservatives in topical applications exposed to UV-light is a serious but poorly understood problem. In this study, a high throughput extraction and selective method based on pressurized liquid extraction (PLE) coupled to gas chromatography–mass spectrometry (GC–MS) was validated and applied to investigate the photochemical transformation of the antioxidant butylated hydroxytoluene (BHT), as well as the antimicrobials triclosan (TCS) and phenyl benzoate (PhBz) in an artificial skin model. Two sets of photodegradation experiments were performed: (i) UV-Irradiation (8 W, 254 nm) of artificial skin directly spiked with the target preservatives, and (ii) UV-irradiation of artificial skin after the application of a cosmetic cream fortified with the target compounds. After irradiation, PLE was used to isolate the target preservatives and their transformation products. The follow-up of the photodegradation kinetics of the parent preservatives, the identification of the arising by-products, and the monitorization of their kinetic profiles was performed by GC–MS. The photochemical transformation of triclosan into 2,8-dichloro-dibenzo-*p*-dioxin (2,8-DCDD) and other dioxin-like photoproducts has been confirmed in this work. Furthermore, seven BHT photoproducts, and three benzophenones as PhBz by-products, have been also identified. These findings reveal the first evidences of cosmetic ingredients phototransformation into unwanted photoproducts on an artificial skin model.

© 2016 Published by Elsevier B.V.

## 1. Introduction

Cosmetics and personal care products (PCPs), such as moisturizing creams, body lotions or sunscreens, are widespread consumer products intended to be in prolonged contact with the skin. Some of the most frequently found cosmetic ingredients exhibit chemical structures capable of absorbing UV-light, thereby undergoing photochemical reactions [1–3]. Hence, it is reasonable to think that these ingredients may undergo certain degree of photochemical transformation when they are applied onto skin areas directly exposed to intense solar radiation.

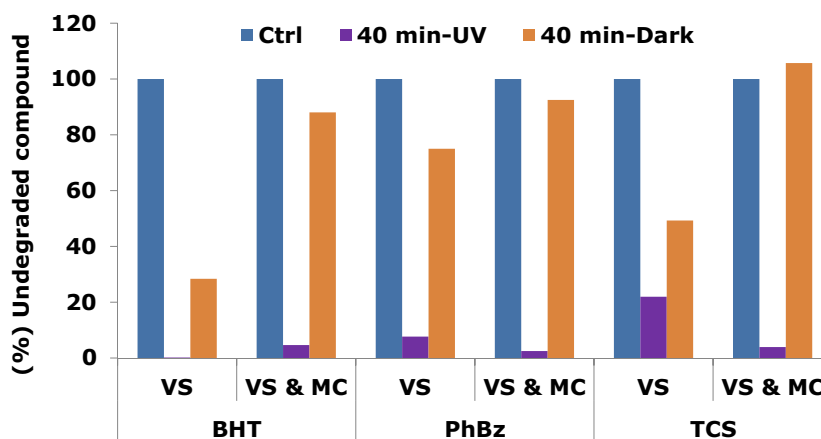
It has been clearly demonstrated that not all UV-absorbers in cosmetic products are sufficiently photostable [4]. Upon UV exposure of topically applied PCPs, cosmetic ingredients can act as photooxidants, via generation of free radicals and reactive oxygen species, when coming into direct contact with the skin [5–7]. Moreover, the reactive intermediates of photounstable ingredients may also behave as photooxidants and may also promote phototoxic or photoallergic contact dermatitis. The interaction of photodegradation products with cosmetic excipients or skin components like sebum may lead to the formation of new molecules with unknown toxicological properties, or even more toxic than the parent compound [8,9]. Consequently, there is an increasing concern about the potential phototoxicity and photoallergy that some cosmetic ingredients may cause, when they are exposed to solar radiation [10].

Due to their practical applications, there is a considerable amount of literature dealing with studies on UV-filters photostability. The behavior of individual filters or final sunscreen products upon UV-light was extensively studied in different works using

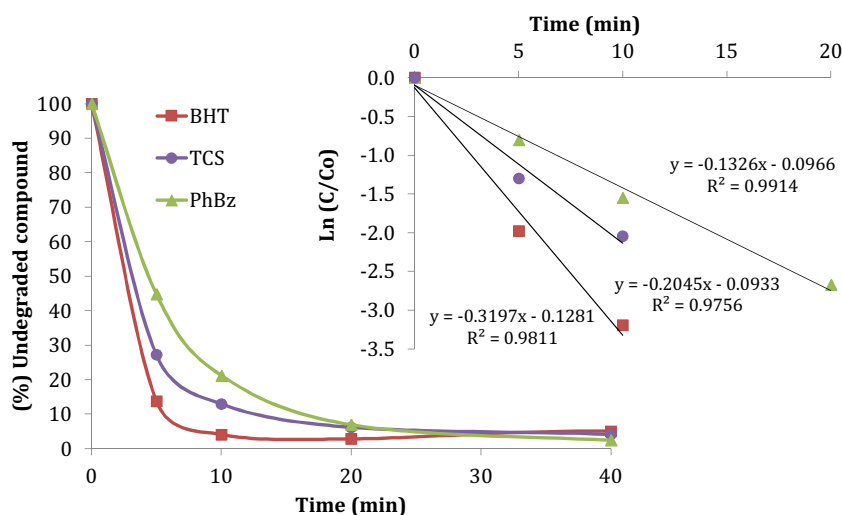
<sup>☆</sup> Selected paper from the XV Scientific Meeting of the Spanish Society of Chromatography and Related Techniques (SECyTA2015) & the VII National Meeting of the Spanish Society of Mass Spectrometry (SEEM2015), 27–30 October 2015, Castellón de la Plana, Spain.

<sup>\*</sup> Corresponding author. Fax: +34 881814468.

E-mail address: [gerardo.alvarez@usc.es](mailto:gerardo.alvarez@usc.es) (G. Alvarez-Rivera).



**Fig. 1.** Influence of irradiation time (40 min 8W-UV) on the target preservatives photodegradation, compared to the control experiment (Ctrl) and the dark test (40 min dark). Comparison of the relative responses obtained in VS (VitroSkin®) and VS&MC (Vitro-Skin® with moisturizing cream) photodegradation experiments.



**Fig. 2.** Photodegradation kinetics of the target preservatives. Linear fit of logarithmic values vs. irradiation time, demonstrating pseudo-first order kinetic behavior.  $C_0$  and  $C$  represent the percentage of undegraded compound at times zero and  $t$ , respectively.

various solar simulators based on xenon-arc lamps or fluorescent lamps [5,11–14]. Nevertheless, the photostability of other ingredients most frequently found in PCPs, such as preservatives, has not been sufficiently investigated so far.

In previous works, the authors studied the phototransformation of several cosmetic preservatives in water and in cosmetic samples, reporting the formation of some relevant photoproducts [3]. Thus, the phenolic antioxidant butylated hydroxytoluene (BHT) was shown to easily photodegrade, rendering several transformation products (TPs) with unknown toxicological properties. The unexpected formation of 2-hydroxy and 4-hydroxybenzophenones, mainly from phenyl benzoate (PhBz), was demonstrated in UV-irradiated personal care products. Furthermore, as expected from previous photodegradation experiments in water [15–17], the photochemical transformation of triclosan (TCS) into 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD) was detected in a real cosmetic matrix under UV-light.

Although it is well documented that triclosan in aqueous solution can be degraded into 2,8-DCDD and other by-products [3,15–19], some discrepancies on dioxin formation can be found in literature regarding the experimental conditions for its generation (mainly pH) [15,20]. The photochemical experiments in cosmetics confirmed that triclosan ring closure reaction can occur under

the conditions of a pH-balanced personal care product, that is, the natural pH of the skin. In this regard, a recent official document reported by the FDA about over-the-counter healthcare antiseptic drugs, states that, although the data support photodegradation in aqueous solution, there is no data regarding whether photodegradation of triclosan can occur on human skin after topical application of triclosan-containing products. Moreover, this document calls for new data regarding the potential for formation of triclosan photodegradation products on human skin as a result of consumer use [21].

The photochemical transformation monitoring of cosmetic ingredients in a biological substrate (e.g., human skin) can be a very challenging issue. The non-targeted screening analysis of possible transformation products, generally occurring at low concentration levels, becomes a complicated task since coelution of matrix components during chromatographic analysis can lead to misinterpretation of mass spectra. Therefore, the use of model substrates (e.g., artificial skin) that mimics the surface properties of human skin, and from which the parent compounds and potential transformation products can be easily recovered, becomes a simpler alternative approach.

Pressurized liquid extraction (PLE) has been recently applied for the analysis of a broad range of cosmetic ingredients such as

Download English Version:

<https://daneshyari.com/en/article/7610104>

Download Persian Version:

<https://daneshyari.com/article/7610104>

[Daneshyari.com](https://daneshyari.com)