Regulatory Toxicology and Pharmacology 72 (2015) 562–568

Contents lists available at ScienceDirect

Regulatory Toxicology and Pharmacology

journal homepage: www.elsevier.com/locate/yrtph

Novel analytical method to measure formaldehyde release from heated hair straightening cosmetic products: Impact on risk assessment

Corrado Lodovico Galli [a,*], Federico Bettin [b], Pierre Metra [b], Paola Fidente [a], Emiliano De Dominicis [b], Marina Marinovich [a]

[a] Section of Risk Assessment, Dipartimento di Scienze Farmacologiche e Biomolecolari, University of Milan, via Balzaretti 9, 20133 Milan, Italy
[b] R&D Department Chelab-Silliker a Mérieux Nutriscience Company, via Fratta 25, 31023 Resana, Italy

ARTICLE INFO

Article history:
Received 25 February 2015
Available online 21 May 2015

Keywords:
Hair smoothing products
Formaldehyde
Analytical method
Fraud control
Cosmetic safety

ABSTRACT

Hair straightening cosmetic products may contain formaldehyde (FA). In Europe, FA is permitted for use in personal care products at concentrations ⩽0.2 g/100 g. According to the Cosmetic Ingredient Review (CIR) Expert Panel products are safe when formalin (a 37% saturated solution of FA in water) concentration does not exceed 0.2 g/100 g (0.074 g/100 g calculated as FA). The official method of reference does not discriminate between "free" FA and FA released into the air after heating FA donors. The method presented here captures and collects the FA released into the air from heated cosmetic products by derivatization with 2,4-dinitrophenylhydrazine and final analysis by UPLC/DAD instrument. Reliable data in terms of linearity, recovery, repeatability and sensitivity are obtained. On a total of 72 market cosmetic products analyzed, 42% showed FA concentrations very close to or above the threshold value (0.074 g/100 g calculated as FA) suggested by the Cosmetic Ingredient Review committee, whereas 11 products, negative using the official method of reference, were close to or above the threshold value (0.074 g/100 g calculated as FA). This may pose a health problem for occasional users and professional hair stylists.

1. Introduction

There are several different types of hair straightening products on the market that can control even the most difficult-to-style hair. Some of the most popular products are specialized shampoos and conditioners, balms, gels, and sprays; these are usually satisfactory for everyday usage. They can help to loosen curls, reducing the amount of heat styling that is needed to blow out or straighten hair. Relaxers and blow-drying aids can make smooth hair last for several days. Such aids include chemicals that break the bonds of the hair, releasing curls and making it easier for hair to remain in a smooth style. The duration of the straightening effect ranges from a few days in-between shampoos to weeks or even months (Kiernan, 2000; Drahl, 2010).

However, the straightening effect can be reversed by environmental factors, mainly contact with water from washing, rain, humidity, etc. Consequently, the most popular products are thermal permanent reconditioning; they use a very strong chemical, formaldehyde (FA), to break the bonds of the hair permanently, forcing it to remain straight and smooth until new hair grows.

FA, in aqueous solution, becomes hydrated to form methylene glycol (MG) (Fox et al., 1985; Kiernan, 2000). MG and FA are in a dynamic balance in favor of MG, following its formation from FA in 70 ms (Boyer et al., 2013).

Long-standing MG polymerizes to form polyoxymethylene glycol. In a neutral-alkaline buffered system, it depolymerizes to methylene glycol that dehydrates into carbonyl formaldehyde. Both the hydrated and non-hydrated forms of FA fix the tissue (Fox et al., 1985). The rate of FA–MG–FA interconversion is a function of temperature. When hair straightening products are heated up to 232 °C/450 F both FA and MG are vaporized along with water (Little, 1999; Gold et al., 1984). As the keratin's action is related to temperature, FA will be rapidly utilized to form bonds. This drives the formaldehyde-methylene glycol toward FA, releasing more FA, hence the faster reaction (Srinivasan et al., 2002). Blow-drying and heat-treating hair with Brazilian hair straightening products (also called Brazilian Keratin Treatment, BKT, Brazilian Blowout, Escova Progressiva, Keratin Cure or Keratin Straightening, etc.)

* Corresponding author.
E-mail addresses: corrado.galli@unimi.it (C.L. Galli), federico.bettin@mxns.com (F. Bettin), pierre.metra@mxns.com (P. Metra), emiliano.de.dominicis@mxns.com (E. De Dominicis).

http://dx.doi.org/10.1016/j.yrtph.2015.05.010
0273-2300/

increase airborne FA, which may represent a risk for professional stylists and customers (Pierce et al., 2011).

The health risk of hair straightening products has been assessed and FA exposure was associated with sneezing and runny nose, headache, irritation of skin, eyes and upper respiratory tract, itchy, red or watery eyes, coughing and sore throat, burning sensation in the eyes, dry itchy skin with rashes, allergic contact dermatitis, nosebleeds (BfR, 2010; McCarthy et al., 2010). Environmental Protection Agency (EPA) considers FA to be a probable human carcinogen and has ranked it in EPA's Group B1 (US-EPA, 1999). The World Health Organization (WHO) International Agency for Research on Cancer (IARC) found sufficient evidence to declare FA a carcinogen (IARC, 2012). In Europe, Canada and Australia, FA is permitted for use in personal care products in non-oral cosmetics, as preservative, at concentration ⩽0.2% (EC, 1976; SCCS, 2011, 2012; HC, 2014; ADHA, 2006; ACCC, 2012). It follows that hair straightening products that are intended to undergo forced convection (for example, blow-drying) and/or heating (for example flat-ironing), processes which cause FA vapors to be created and released are not allowed to contain more than 0.2%. Products containing >0.05% FA must be labeled "contains formaldehyde." These limits are expressed as "free formaldehyde" or "calculated as formaldehyde." The US Cosmetic Ingredient Review (CIR) Expert Panel suggested that FA and methylene glycol are safe for use in personal care products, provided that they are formulated to ensure use at the minimal effective concentration, but in no case should the formalin concentration exceed 0.2% (w/w), which would be 0.074% (w/w) calculated as formaldehyde or 0.118% (w/w) calculated as methylene glycol (CIR, 2011). However USFDA analysis of approximately 50 mg of Brazilian Blowout confirmed the presence of methylene glycol, the liquid form of formaldehyde, at levels ranging from 8.7% to 10.4% (FDA Brazilian Blowout Warning Letter, 2011). The concern of the Authorities rests on the evidence that although in hair straightening products the concentrations of FA should be confined to a maximum of 0.2%, the present survey conducted by our laboratory has shown that the concentrations of FA exceed 3%, a finding confirmed by the analyses done by the Chemisches und Veterinäruntersuchungsamt (CVUA), which found FA concentrations ranging from 0.42% to 5.83% in 7 of 10 hair straightening products used in Germany (Monakhova et al., 2013) and by the Oregon Occupational Safety and Health Administration, which measured FA concentrations in 105 hair straightening products from 54 salons, finding average concentrations ranging between 1.2% and 8.8%. More than one-third of the samples came from Brazilian Blowout Acai Professional Straightening Solution bottles labeled "formaldehyde-free," notwithstanding the fact that their FA content ranged from 6.8% to 11.8%, averaging more than 8% (McCarthy et al., 2010).

Health Canada pulled Brazilian Blowout's products off the market, after finding that their formulas contained more than 8% FA, which is 42 times the acceptable limit when it is used as a preservative in some cosmetic products (HC, 2010).

Currently available analytical methods measure FA concentration derivatizing at room temperature the FA values present by using 2,4-dinitrophenyl hydrazine (DNPH) to form formaldehyde-DNPH, which is then detected by direct HPLC/DAD analysis (Soman et al., 2008) or as FA by ^{1}H NMR determination (Monakhova et al., 2013). The procedure proposed in this paper is effective in capturing and collecting also FA released into the air from FA donors when straightening products are heated up to 232 °C/450 F, following derivatization with DNPH and final analysis by UPLC/DAD instruments. Good data in terms of linearity, recovery, repeatability and sensitivity are obtained.

2. Materials and methods

2.1. Chemicals and apparatus description

Acetonitrile HPLC gradient-grade and hydrochloric acid 37% (wt.) ACS reagent grade were supplied by Sigma Aldrich (Milwaukee, WI, USA), while ultra-pure water was used throughout the experiments (MilliQ system, Millipore, Bedford, MA, USA).

The other HPLC-gradient grade reagents such as Formaldehyde (39.4% solution in water), sodium phosphate monobasic and sodium phosphate dibasic were also purchased from Sigma Aldrich, DNPH was from Aldrich Chemical Company Inc. Glass vials with septum screw caps were supplied by Agilent Technologies (Santa Clara, CA, USA).

The extraction/derivatization apparatus (Fig. 1) was composed of a 250 mL test tube (A) placed into a heating digester DK 20 from Velp Scientifica (Usmate, Italy) (B) with temperature between 130 and 240 °C ± 1.5 °C. and equipped with a glass bubbler connected to a nitrogen manifold (the bubbler was placed 5 cm upon the sample position); the exit line (C) was routed through a 250 mL Drechsel's bottle containing the derivatization solution (D) by 6 mm diameter glass connections and a bubbler equipped with porous septum (E). The derivatization solution is placed at 5°C in an ice bath.

Nitrogen, supplied as liquid nitrogen 99.997% by AirLiquide (Paris, France), was used as carrier gas (to drive formaldehyde through test tube with sample and to allow the bubbling inside the extraction/derivatization solution). It was kept at room temperature with a constant flow of 0.5 m^3/h.

Stock FA solution at a concentration of 40 mg/mL was prepared using acetonitrile as the solvent.

Derivatization solution of DNPH at 8 mg/mL was prepared in hydrochloric acid/water 70/30 w/w.

Hair-straightening products analyzed were commercially available (51) or withdrawn from the Italian market (21) by inspection authorities (Guardia di Finanza, Brescia, Italy).

2.2. Cosmetic product preparation

0.5 g of cosmetic was weighed at the bottom of the 250 mL test tube. The reaction flask was filled with 20 mL of 4 mM DNPH

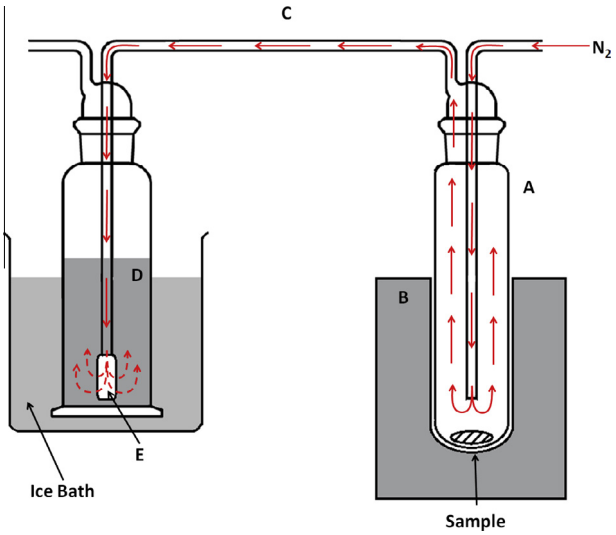

Fig. 1. Schematic representation of the extraction/derivatization apparatus composed by a 200 mL test tube with cosmetic product on the bottom (A) placed in an heating digester (B). The test tube is connected by 6 mm diameter glass connection (C) and a porous septum (E) through a derivatization flask (D) placed in an ice bath.