SOLID-PHASE EXTRACTION PROCEDURE FOR THE ASSAY OF 1,4-DIOXANE IN COSMETIC PRODUCTS

S. Scalia and G. Frisina(1)

Department of Pharmaceutical Sciences
University of Ferrara
via Scandiana 21
44100 Ferrara
Italy

(1)Himont Research Centre
Ferrara
Italy

SUMMARY

Cosmetic preparations containing polyethoxylated surfactants can be contaminated by 1,4-dioxane. This substance has been shown to be carcinogenic to rats and mice and has been considered as a possible carcinogen in humans. According to the EEC directive on cosmetic products, 1,4-dioxane must not be present in their formulation. Published methods for the assay of this substance in cosmetics are based on gas chromatography (GC) or headspace GC. These techniques have distinct disadvantages including complex and time-consuming sample pre-treatment, extensive calibrations, poor accuracy and precision. Improved recovery and reproducibility have been attained by a recently developed HPLC method; however this technique exhibits a low sensitivity. This study describes a new solid-phase extraction procedure for the determination of 1,4-dioxane in cosmetic preparations. After purification by Bakerbond C18 and CN cartridges, samples were directly analysed by HPLC and GC-MS. The proposed method is rapid, reproducible and suitable for routine quality control analyses. The application of the procedure to the assay of 1,4-dioxane in a wide range of commercially available surfactants and cosmetic products is also reported.

INTRODUCTION

Polyethoxylated derivatives are the most widely used surfactants in shampoo and bath preparations [1] and are commonly contained in other cosmetic products [2]. 1,4-dioxane may be formed during the polymerisation of ethylene oxide to produce the polyoxyethylene moiety of the emulsifiers [3,4]. Hence, cosmetics containing ethoxylated surfact-
ants may be contaminated by 1,4-dioxane [5,7], a carcinogen in rats and mice [8,9] which is absorbed through the intact skin of animals [10]. Furthermore, 1,4-dioxane has been classified as a possible carcinogen in humans [11,12]. According to the EEC directive on cosmetics [13], 1,4-dioxane must not be present in their formulations. Consequently the assay of this substance in the surfactants, used as raw materials for the production of cosmetics, and in the finished product is of direct concern to consumers.

Classical methods for the quantitative determination of 1,4-dioxane in cosmetic matrices are based on gas chromatography (GC) [4,14,15] or headspace GC [6,16,17]. These techniques, however, have distinct disadvantages such as complex and time consuming sample pre-treatment [4,14] extensive calibrations [6,16,17], the need for prolonged equilibrium times [6], unsatisfactory reproducibility [14,15] and a high degree of variability in the recovery values obtained from different cosmetic formulations [14]. For routine determination of 1,4-dioxane in cosmetics, an accurate, precise and simple method was required. This study reports on the development of solid-phase extraction procedures for the rapid and efficient purification of the complex cosmetic matrices before assay of 1,4-dioxane by reversed-phase high-performance liquid chromatography (RP-HPLC) and GC-mass spectrometry (GC-MS). The application of these methods to the determination of 1,4-dioxane in commercial surfactants and finished cosmetic products is also reported.

EXPERIMENTAL

Materials

HPLC-grade 1,4-dioxane, hexane, dichloromethane, acetonitrile and water were supplied by Farmitalia Carlo Erba (Milan, Italy). Bakerbond C-18, Bakerbond Si and Bakerbond CN cartridges were obtained from J T Baker (Phillipsburg, NJ, USA). Surfactant samples were from commercial suppliers. The nomenclature of the Cosmetic, Toiletry and Fragrance Association (CTFA) Cosmetic Ingredient Dictionary [18] has been used throughout. Commercial cosmetics, containing polyoxyethylated surfactants, were from retail stores or from manufacturers or importers of these products.

Chromatography

The HPLC apparatus consisted of a Jasco chromatographic system (Model 880-PU pump, Model 880-02 ternary gradient unit and Model 875 UV/VIS detector; Jasco, Tokyo, Japan) linked to an injection valve with a 20μl sample loop (Rheodyne, Cotati, CA, USA) and a chromatographic data processor (Chromatopac C-R3A, Shimadzu, Kyoto, Japan). The detector was set at 200 nm and 0.01 absorbance units full scale. Sample injections were made with a Hamilton 802 RN syringe (10-μl; Hamilton, Bonaduz, Switzerland).

Separations were performed on a LiChrospher CH-8 column (5-μm, 250 x 4.0 mm i.d.; Merck, Darmstadt, FRG) under gradient conditions at a flow-rate of 1.0 ml/min. Solvent A was 5% (v/v) acetonitrile in water and solvent B was 50% (v/v) acetonitrile in water. The elution programme was as follows: isocratic elution with 5% solvent B, 95% solvent A for 5 min, then a 2-min linear gradient to 95% solvent B; the mobile phase composition was finally maintained at 95% solvent B for 1 min. Samples were injected 0.5 min after the start of the elution programme. The mobile phase was filtered through type HVLP filters (0.45-μm; Millipore S.A., Molsheim, France) and on-line degassed by a model ERC-3311 automatic solvent degasser (Erma, Tokyo, Japan). Chromatography was carried out at ambient temperature. Peak areas were quantified using the integrator which was calibrated with standard solutions of pure 1,4-dioxane.