

化粧品の 글리콜類 및 글리세린 함량에 관한 研究

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Determination of glycols and glycerin in cosmetic products

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==Abstract==

The rapid determination of propylene glycol, 1,3-butylene glycol, and glycerin in fifty five cosmetic products marketed were carried out by gas chromatographic procedures. The samples were mixed with methanol by ultrasonificate mixture, then the mixed materials were filtered or centrifuged. The transparent filtrate or supernatant was analyzed by gas chromatography using a tanax GC column.

The results were as follows;

1. Glycol and/or glycerin were detected in thirty two samples (58.2%). Among them, propylene glycol and glycerin were detected together in twelve samples (21.8%), propylene glycol alone in fourteen samples (25.5%), glycerin alone in five samples (9.1%), but 1,3-butylene glycol alone in only one sample.
2. The concentration of propylene glycol was 0.4~16.5% w/w, glycerin was 0.8~11.7% w/w, and 1,3-butylene glycol was 6.7% w/w.

緒論

化粧品에는 프로필렌 글리콜(propylene glycol)과 1,3-부틸렌 글리콜(1,3-butylene glycol) 등의 글리콜類와 글리세린(glycerin)이 化粧品 原料 基準에 收載되어 保濕劑, 保濕性 溶劑 또는 乳化劑로 使用되며 글리콜類는 抗菌의 作用이 認定되고 있다.¹⁾ 이 중 프로필렌 글리콜과 글리세린은 食品添加物公定書나 大韓藥典에도 收載되어 醫藥品이나 食品에서 色素, 香料 등의 溶劑로도 쓰여지고 있으나^{2,3)} 이들에 對한 使用量이나 標記에는 아무런 規制나 義務는 없다. 이에 著者等은 우선 韓國產 化粧品類에 있어서 이들 成分의 使用 實態를 調査하고자 이 實驗을 하였다. 글리콜類와 글리세린의 同時分析法으로는 薄層크로마토그래프法,⁴⁾ 紫外部吸收分光光度法, 高速液體크로마토그래프法⁵⁻⁸⁾, 가스 크로마토그래프法⁹⁻¹⁶⁾의 많은 方法으로 食品等

에서 報告되고 있으나 化粧品이나 醫藥部外品같이 여러 種類의 成分의 混合物로 되어있는 境遇에 迅速하게 同時 定量할 수 있는 tenax GC column에 依한 가스 크로마토그래프法을 利用하여 6種類 49件의 化粧品과 齒藥 6건에 對하여 分析한 結果를 報告코져 한다.

材料 및 方法

1. 材料

1985년 1월 부터 11월 사이에 市中에서 流通되고 있는 크림 13件, 乳 로오션 5件, 스킨 로오션 5件, 샴푸 9件, 헤어린스 9件, 립스틱 8件과 치약 6件 등 55件.

2. 試藥

propylene glycol (Kanto chemical Co., INC., GR), 1,3-butylene glycol (Wako pure chemical Industries LTD, GR), glycerin (Duk san pharmaceutical Co., LTD, GR), ethylene glycol (Kanto chemical Co.,

INC, GR), methyl alcohol (Junsei chemical Co., LTD, GR), tenax GC (Alltech Associates INC., 60~80mesh).

3. 機器

Ultrasonic generator (Bransonic 220), 遠心分離器 (第一理化學器機製作所, Model C-C₈), Gas chromatograph (Shimadzu GC 8A).

4. 測定條件

가스크로마토그래프에 의한 測定條件은 다음과 같았다. Column은 tenax GC (ϕ 2mm id \times 2m, stainless steel, 60~80 mesh)로 새로 充填하여 約 8時間 280°C에서 前處理한 後 使用하였으며, Column 온도는 70°C, Injector 온도는 300°C, detector는 FID, carrier gas는 Nitrogen, sample size는 3.0~5.0 μ l이었다.

5. 分析方法

① 標準液의 調製—propylene glycol, 1,3-butylene glycol 및 glycerin 各 約 1g씩을 精密히 取하여 各 50ml메스후라스크에 넣고 methyl alcohol에 溶解하여 50ml로하여 標準原液으로 하고 이 液 5ml, 10ml, 20ml 및 內部標準液 1ml을 加하여 100ml가 되게한다.

② 檢液의 調製—試料 約 1g을 精密히 달아 50ml 메스후라스크에 넣고 methyl alcohol 30ml를 加하고 잘 混和하고 化粧水等은 잘 混들어 섞고 크림, 샴푸, 헤어린스, 립스틱, 치약 등의 試料는 ultrasonic generator로 25°C에서 15分~1時間씩 抽出하고 各 各에 內部標準液 1ml씩을 加한 後 methyl alcohol로 눈금을 채우고 잘 混들 섞어 濾過 또는 遠心分離 (3,000 rpm, 10分間)하였다.

③ 內部 標準物質로는 ethylene glycol을 約 5g을 달아 100ml로 한 後 1ml 씩을 使用하였고 定量은 peak height ratio 法으로 測定하였다 (Fig. 1).

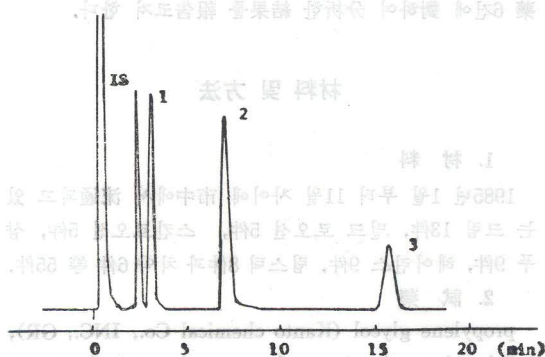


Fig. 1. Gas chromatogram of glycols and glycerin. 1S, ethylene glycol; 1, propylene glycol; 2, 1,3-butylene glycol, 3, glycerin.

實驗結果 및 考察

1. 抽出條件의 選擇

抽出溶媒는 립스틱 類를 除外하고 methyl alcohol 使用時抽出率이 매우 良好하였으며 抽出溫度는 30°C, 抽出時間은 15分에 100%抽出되었으나 립스틱類는 글리콜類나 글리세린이 전혀 檢出되지 않으므로 1時間以上까지도 抽出을 試圖하였다.

2. 檢量線의 作成

propylene glycol과 1,3-butylene glycol은 0.5, 1.0, 2.0, 4.0, 8.0mg/ml로 glycerin은 1.0, 2.0, 4.0, 8.0mg/ml가 되도록 標準原液을 稀釋하고 內部標準液은 ethylene glycol溶液 (50mg/ml) 1ml를 標準液 50ml에 對하여 加하였다. 上記의 gas chromatography 條件에서 測定하여 檢量線을 作成한 結果 良好한 直線關係를 나타내었다 (Fig. 2).

3. 回收率과 再顯性

propylene glycol과 1,3-butylene glycol 및 glycerin이 檢出되지 않거나 最少로 檢出된 製品 7種을 選擇하여 各 1g씩을 取하여 propylene glycol 標準原液 1ml, 1,3-butylene glycol 標準原液 2ml, glycerin 標準原液 4ml씩을 正確히 加하여 上記의 gas chromatography 條件에서 測定한 結果 回收率과 再濕性은 良好하였다 (Table II).

4. 市販

化粧品中 크림 13件, 밀크로오션 5件, 스킨로오션 5件, 샴푸 9件, 헤어린스 9件, 립스틱 8件과 齒藥 6件等 55件에 對하여 글리콜類와 글리세린 含量을 分析한 結果 檢出된 것은 32件이었으며 크림과 밀크로오션은 18件모두에서 檢出되었으며 大部分이 propylene glycol

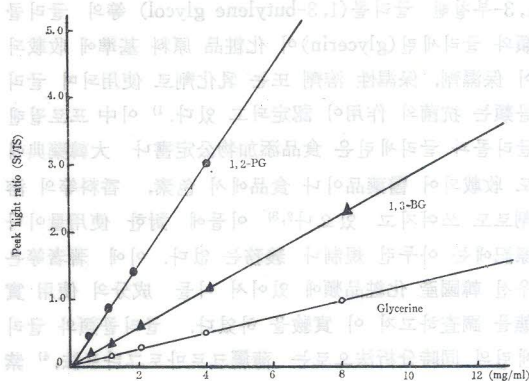


Fig. 2. Calibration curve of propylene glycol, 1,3-butylene glycol and glycerin.

Table I. Analytical result of glycols and glycerin in cosmetic samples.

Sample	No. of Samples	No. of Samples detected	No. of detected Samples and Analytical Result (% , min. ~ max.)		
			Propylene glycol	1,3-Butylene glycol	Glycerin
Cream	13	13	12(1.7~ 6.6)	1(6.7)	6 (0.9~ 6.7)
Milk lotion	5	5	3(4.2~16.5)	0 (-)	4 (3.2~11.7)
Skin lotion	5	3	3(4.5~ 7.8)	0 (-)	3 (3.0~ 8.3)
Sham poo	9	4	3(0.6~ 1.8)	0 (-)	2 (0.8~ 1.9)
Hair rinse	9	5	5(0.4~ 1.6)	0 (-)	0 (-)
Lip stick	8	0	0 (-)	0 (-)	0 (-)
Tooth paste	6	2	0 (-)	0 (-)	2(10.2~10.7)
Total	55	32	27(0.4~16.5)	1(6.7)	17 (0.8~11.7)

Table II. Recoveries of glycols and glycerin added to cosmetic products.

Sample	Recovery (% , Mean±SD)		
	Propylene glycol	1,3-Butylene glycol	Glycerin
Cream	104.20±4.85	97.26±3.22	102.68±2.06
Milk lotion	98.24±2.80	98.42±1.42	101.04±3.84
Skin lotion	98.56±2.04	96.75±2.45	98.30±1.92
Shampoo	101.02±1.88	97.90±2.25	102.12±2.14
Hair Rinse	98.32±1.81	98.55±1.75	98.62±3.93
Lip stick	103.71±4.86	95.85±2.94	103.12±2.07
Tooth paste	104.92±2.53	95.78±3.28	98.17±3.05
Added amount(mg/g)	20	4	80

과 glycerin을單獨 혹은 併用한 것으로 나타났고 1,3-butylene glycol은 cream 1件에서만 單獨으로 檢出되었다. 스킨로오손은 5件中 3件에서 propylene glycol과 glycerin의 併用으로, 샴푸에서는 9件中 4件에서 propylene glycol과 glycerin 單獨 혹은 併用으로 헤어 린스는 9件中 5件에서 propylene glycol이 單獨으로, 치약은 6件中 2件에서 glycerin이 單獨으로 檢出되었고 립스틱은 8件中 1件에서도 檢出되지 않았다(Table I).

한편 propylene glycol의 檢出濃度は 27件에서 0.4~16.5% w/w, glycerin은 17件에서 0.8~11.7% w/w, 그리고 1,3-butylene glycol은 1件에서 6.7%w/w이었다.

結 論

1985年 1月~11月中에 서울市中에서 流通되는化粧品과 齒藥等 試料 55件에 對하여 gas chromatography에

來하여 글리콜類와 글리세린 使用實態를 調査한 結果 32件에서 使用한 것으로 나타났으며, 그中 大部分은 propylene glycol과 glycerin으로 單獨 또는 併用으로 使用濃度は propylene glycol은 0.4~16.5% w/w, glycerin은 0.8~11.7% w/w이었고 1,3-butylene glycol은 거의 使用되지 않는 傾向이었다.

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編 註