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Determination of Formaldehyde in Cosmetics by HPLC Method and Acetylacetone Method

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ABSTRACT

This paper describes an assay method to determine free formaldehyde in cosmetics using High Performance Liquid Chromatography (HPLC), with a pre-column derivation with 2,4-dinitrophenylhydrazine. The derivatives were analyzed using a RP_8 column with 45% acetonitrile solution as mobile phase and detected at the wavelength of 345 nm. The detection limit of derived formaldehyde in this HPLC system was 0.2 ppm. Compared with the amounts of formaldehyde analyzed from the 0.2% formaldehyde donors, the results obtained by acetylacetone method were 1.62~17.35 times higher than that of HPLC method. One hundred cosmetic products purchased during 1995-1996 were investigated. None of those products was labeled formaldehyde. The results showed that 53% of the samples were formaldehyde positive. The amounts of total free formaldehyde were between 3~165 ppm. All of them were less than 1000 ppm.

Key words: Cosmetics, formaldehyde, formaldehyde donor, HPLC, acetylacetone

INTRODUCTION

Formaldehyde is a colorless solution with pungent smell. 37% formaldehyde water solution is called formalin. People who inhale formaldehyde gas get congested and have breathing difficulty in some sever cases. Mice which inhale 15 ppm formaldehyde for 18 months easily get tumor in the respiratory tracts[1].

Different countries have different regulatory practices for cosmetics, in which formaldehyde is used as a preservative. Japan, Thailand and our country inhibit the direct use of formaldehyde in cosmetics because it is highly biocidal, pungent and skin-irritant, being used in cosmetics directly. Limitation of formaldehyde content in Europe Union is 0.2%. USA, Australia and New Zealand have no regulation on formaldehyde. In the southeastern Asia, Singapore, Malaysia, Indian and Hong Kong still use formalin in cosmetics[2,3]. The regulation of formaldehyde donor (or formaldehyde releasing preservative) in cosmetics also differs from country to country, as shown in Table 1[4,5,6,7]. Since FDA in USA has no regulation on content of formaldehyde and formaldehyde donor in cosmetics, the Cosmetic, Toiletry and Fragrance Association (CTFA) recommends amount for preservatives. European Union (EU) suggested that maximum amount of 6 preservatives in cosmetics should be around 0.1~0.6%. For formaldehyde, 0.2% is allowed[3,4,5]. In Japan, limited imidazolidinyl urea and DMDM hydantoin is allowed to be added in rinse-off cosmetics, such as shampoo, rinse lotion, body wash, facial cleanser and other cleaning lotion after Oct, 1995[6]. In Taiwan, three formaldehyde donors, quaternium 15, glydant and imidazolidinyl urea, were regulated to contain free formaldehyde less than 1000 ppm after July, 1998[7].

Various methods were applied to detect the concentration of formaldehyde in cosmetics. Conway cell microdiffusion apparatus with fluorescent illumination was employed in the early days[8]. Analytic methods such as polarography[9], thin layer chromatography, colorimetry by reacting formaldehyde with chromotropic acid, 2,4-dinitrophenylhydrazine or acetylacetone[10,11,12], HPLC[13,14,15,16,17] and even MASS spect were developed over the years[18].

In this article, we discuss ways to detect free formaldehyde in cosmetics by HPLC or Acetylacetone methods and compare them in five formaldehyde releasers' cases. We also detect the formaldehyde content in 100 commercial cosmetics in the market during 1995 to 1996.

MATERIAL AND METHODS

I. *Samples*

100 cosmetic products were purchased from department stores, supermarkets, grocery stores and cosmetic

Table 1. Approval in US, EC, Japan and ROC

CTFA Name	Trade Name	US[a]	EC	Japan[c]	ROC[d]
Imidazolidinyl Urea	Germall 115	SAU[b]	0.6%	0.3%	0.6%
Diazolidinyl Urea	Germall II	0.5%	0.5%	NA	NA
DMDM Hydantoin	Glydant	SAU	0.6%	0.3%	0.6%
Quaternium 15	Dowilcil 200	SAU	0.2%	NA	0.2%
Bronopol		0.1%	0.1%	NA	NA
Formalin		0.2%	0.2%	NA	Forbidden

a: suggested by CTFA b: sale as used c: rinse off products only
d: the total content of free formaldehyde should not be more than 1000 ppm, when these formaldehyde donors are used as preservatives in cosmetics
NA: not available

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shops in Taipei during 1995 – 1996. Among them, there were 46 domestic products including 22 leave-on and 24 rinse-off products; and 54 imports including 28 leave-on and 26 rinse-off products. No products were labeled 'formaldehyde-contained' in these 100 cases. 20 were labeled containing formaldehyde donors (such as diazolidinyl urea, imidazolidinyl urea, quaternium 15, DMDM hydantoin and bronopol) including 2 domestics and 18 imports (Table 2).

II. *Reagents and Equipment*

(I) *Reagents and solutions*

Five formaldehyde donors were bronopol, diazolidinyl urea, imidazolidinyl urea, quaternium 15 (from Sigma, US) and DMDM hydantoin (from Lonza, US). Other reagents were in analytical or better grade. Relative solutions were prepared as follow:

(1) Formaldehyde standard solution

Proper amount of 37% formaldehyde solution was diluted with water to 2, 4 and 8 ppm to be standard solutions.

(2) Acetylacetone solution

Ammonium acetate of 150 g was dissolved in water, followed by adding 3 mL of acetic acid and 2 mL of acetylacetone and diluting with water again to a total volume of 1000 mL.

(3) Ammonium acetate solution

It was prepared in the same way as described above (Material and Methods II (I) (2)) but without adding acetylacetone.

(4) 0.1% 2,4-dinitrophenylhydrazine

One tenth gram of 2,4-dinitrophenylhydrazine (2,4-DNPH in short) was dissolved in 80 mL of 2 N hydrochloric acid in a 100 mL volume flask and further diluted with water to the volume.

(5) Tetrahydrofuran solution

Tetrahydrofuran solution was prepared by Tetrahydrofuran (THF for short) and deionized water in ratio 9:1 (v/v) ratio.

(II) *Equipment*

One HPLC instrument (Shimadzu LC6A) was equipped with UV detector (Shimadzu SPDM6A) and integrator (Shimadzu CR4A). The other one (Shimadzu LC6A) was connected to Shimadzu photodiode array M10A and computer implements (such as Acer 386SX).

Spectrophotometer (Milton Roy Spectronic 3000) was used in Acetylacetone colorimetry method.

Table 2. Labeling and source of cosmetic samples

Source	Leave on	Rinse off	Total
	Formaldehyde donor labeled / sampled		
Domestic	1/22	1/24	2/46
Imported	12/28	6/26	18/54
Total	13/50	7/50	20/100

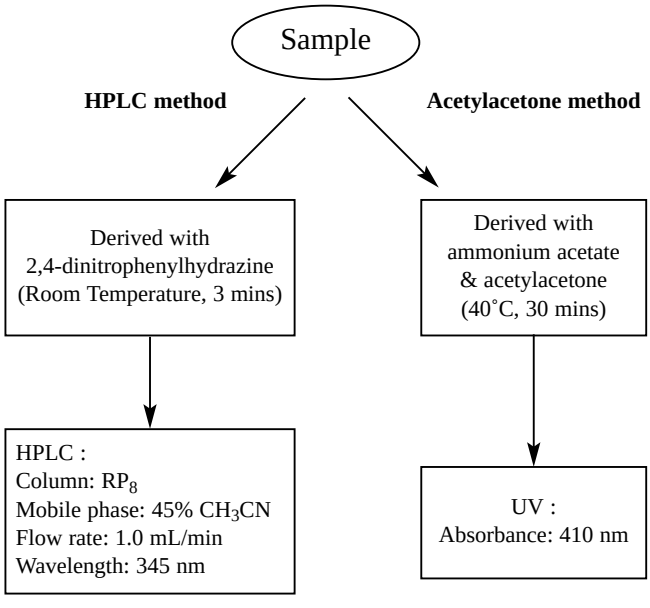

Figure 1. Flow chart of formaldehyde analysis

III. *Methods*

Two parts of the experiment procedures are addressed here which were done by HPLC and acetylacetone colorimetry analyses (Figure 1) respectively. They are described as following:

(I) *HPLC analysis of free formaldehyde*

The modified protocol to detect free formaldehyde in cosmetics by HPLC based on the method suggested by Benassi *et al.*[13] (1989) is described below:

(1) Sample preparation

One gram of sample was dissolved in Tetrahydrofuran solution. For those not dissolved, little Triton X-100 was added as cosolvent. Solutions were shaken to homogeneity and diluted properly for further use.

(2) Derivative procedure

One mL of solution described above was mixed with

0.45 mL of 0.1 N 2,4-DNPH on a vibrator for a few minutes. The solution was then mixed with 0.4 mL of 0.1 M phosphate buffer (pH 6.8) and 1.4 mL of 1 M sodium hydroxide for serving as the sample solution.

(3) Analytic condition of HPLC

A 10-μL sample solution was analyzed with a Licrosorb RP_8 (250 × 4 mm, 10 μm, Merck) column with 45% acetonitrile solution as mobile phase and detected at the wavelength of 345 nm. The flow speed was 1.0 mL/min.

(4) Standard curve

After titration by the method described in Material and Methods III. (I) 7, formaldehyde standard solution was prepared into 0, 2, 4, 8 and 16 ppm solutions by diluting in tetrahydrofuran solution. After derivation and analysis via HPLC as described in Material and Methods III. (I) 2 and 3, we plotted peak area versus concentration to get the standard curve.

(5) Qualification and quantification of formaldehyde

Sample derivatives were analyzed in HPLC and compared with the retention time of standard formaldehyde for qualification. Peak area of sample solution was substituted in the calibration equation of standard curve, which we derived from the procedure described in Material and Methods III. (I) 4, in order to calculate the concentration of formaldehyde.

(6) Recovery calculation

Formaldehyde solution was added to shampoos, creams and lotions, in which the formaldehyde concentration was diluted to 2~8 ppm by tetrahydrofuran. According to Material and Methods III. (I) 5, we obtained the concentration of formaldehyde in samples and compared these with the known add-in concentration to calculate the recovery.

(7)Formaldehyde titration[9]

One gram of formaldehyde solution was diluted with water into 100 mL. 10 mL of which was added to 50 mL of 0.1 N iodine and 20 mL of 1 N potassium hydroxide. The solution was then put in the dark for 15 minutes before 5 mL of 30% sulfuric acid solution was added. The excessive iodine was titrated by 0.1 N sodium thiosulphate (indicator solution was 1 mL starch solution). Blank test was done using 10 mL of water to calculate the background 0.1 N sodium thiosulphate consumption. Each mL of titrated 0.1 N iodine was equal to 1.5013 mg formaldehyde.

$$\text{HCHO} = \frac{1.5013 \times (\text{Vo-V}) \times \text{F}}{\text{WS}} \times 100\%$$

HCHO: formaldehyde (%)

V : depleted 0.1 N sodium thiosulphate solution (mL)
Vo : depleted 0.1 N sodium thiosulphate solution (mL) in blank experiment
F : Valence of 0.1 N sodium thiosulphate solution
WS: formaldehyde solution (g)

(II) *Quantification of formaldehyde by acetylacetone colorimetry*[10]

Sample (1 g) was weighed and put in centrifuge tube. After 20 mL of 25% sodium sulfate was added, the tube was shaken and water was added to make the whole volume as 40 mL. Then the tube was water-bathed at 40˚C for 1 hour, cooled down, and centrifuged at 3500 rpm for 10 mins. Then the supernatant was filtered. Two samples of each 5 mL were taken from the filtrate. Sample I: 5 mL acetylacetone solution was added. Sample II: 5 mL of ammonium acetate solution was added. Both samples were water-bathed at 40˚C for 30 mins and cooled down for 30 mins. Absorbance was measured at 410 nm for both samples of (AI and AII). 5 mL of formaldehyde standard solutions in the three different concentrations described in Material and Methods II. (I). 1 and 5 mL of water were treated in the same way as described above. Their absorbance were designated as As1~As3 and Ao, respectively. Formaldehyde standard curve in this acetylacetone colorimetry approach was constructed by plotting (As-Ao) versus concentration. Solution concentration can be obtained by substituting the absorbance of (AI-AII) into equation of standard curve. Formaldehyde content in samples was calculated by multiplying the concentration with the volume and dividing by the sample weight.

RESULT AND DISCUSSION

I. *Analysis of Free Formaldehyde in Cosmetics by HPLC*

According to the suggestions in literature and facilities available in regular laboratories, we used derivation colorimetry first and then detected free formaldehyde by HPLC in this study. According to the method provided by Benassi *et al.*[13], formaldehyde standard solution was given color from the derivation reaction with 2,4-DNPH first and then subject to flow through C_8 column where acetonenitrile and water (1:1, v/v) were served as mobile phase. The flow speed was 1.0 mL/mins. Sample was detected at the wavelength of 345 nm. The formaldehyde peak, which had retention time of 10.97 mins, was detected as a single peak at wavelength 345 nm. When it was detected at UV 254 nm, there was a small tailing peak coinciding with it. The small peak can be separated from the main peak by changing the mobile phase composition to acetonenitrile and water in a ratio 45:55(v/v) at the wavelength fixed at 345 nm, and reduced the other noise as well (Figure 2).

(I) *Reaction condition of derivation*

(1) Dilution effect

Matrix effect was discussed when we diluted the shampoo sample, which contained 0.1% formaldehyde, to 10 or 50 folds. The recovery rate of a 10-fold dilution was found to be 80.40% while that of 50-fold dilution was 93.78%. We took 50-fold dilution for all the samples (Table 3).

(2) Derivation time

The derivation time of sample solution with 2,4-DNPH was plotted against its corresponding peak area. As shown in Figure 3, the maximal value can be obtained in three minutes. The derivation protocol that Benassi *et al*.[13] suggested was one-minute shaking and two-minute standing. For convenience, we shook samples for three minutes without standing them. The ANOVA analysis showed that there was no difference between these two methods (data not shown). Hence, we derived our samples by shaking for three minutes in this study

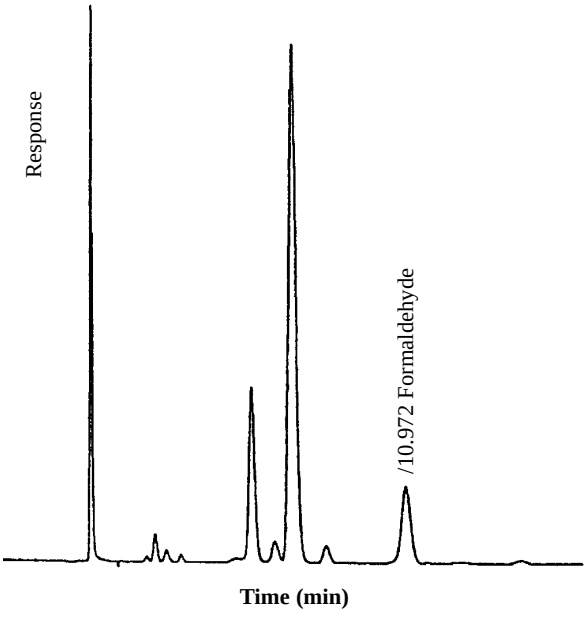

Figure 2. HPLC chromatogram of formaldehyde derivated with 2,4-DNPH.

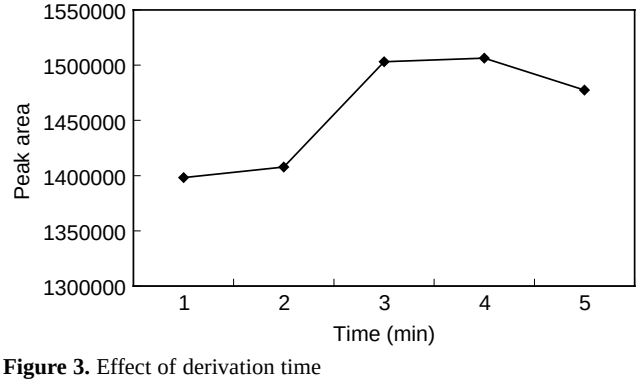

Figure 3. Effect of derivation time

Table 3. Matrix effect of shampoo with ten and fifty times dilution in the formaldehyde assay

Dilution factor	Recovery (%)	C.V. (%)
50	93.78	4.53
10	80.40	2.98

(3) Stability of derivative

It was found that the longer derivatives stayed before injection, the less derivative remained. After two hours, the left derivative was only around 54% (Figure 4).

(4) pH influence on the stability of hydrazone derivatives from 2,4-DNPH

Derivatives needed to be analyzed soon after the reaction due to instability, which caused the operational difficulty. It was found pH value had tremendous effect on the stability of derivatives. From Benassi's approach[13,21], solution pH is under 2 after reaction. Only around 66.03% of the derivatives remained after 40 minutes. To improve instability of the compounds, we added 1.4 mL of 1M sodium hydroxide, and pH was adjusted to 4.5~6. An enhanced stability of derivatives was observed while no obvious degradation (99.99~106.26%) was found in 40 minutes (Figure 5). But in over-elevated pH, the derivative solution turned red instead of yellow and particles started to generate over the filtration screen, which cause blockade in the injection needle and chromatograph loops.

(II) *Standard curve and recovery*

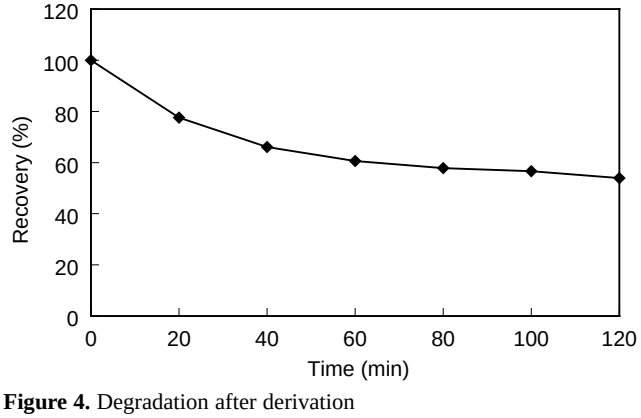

Figure 4. Degradation after derivation

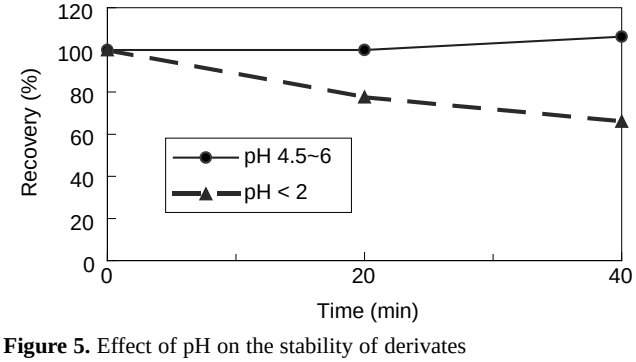

Figure 5. Effect of pH on the stability of derivates

According to Material and Methods III. (I) 4, the standard curve we got had relative coefficient of 0.9993. Based on the illustration in Material and Methods III. (I) 6, the recovery and relative coefficient of calibration curve for shampoos were 90.3 – 98.7% and 0.9989 respectively, while those for creams were 93.5 – 95.6% and 0.9913 respectively and those for lotions were 92.9 – 97.7% and 0.9999. The lowest detectable amount was 0.2 ppm (base on if S/N ratio is larger than 10). Benassi *et al.*[13] also got similar detection limit of 0.2 ppm (S/N ratio is larger than 2).

II. *Detection of Formaldehyde from Formaldehyde Donors by Acetylacetone Colorimetry Detection*

Five formaldehyde donor solutions (diazolidinyl urea, imidazolidinyl urea, quaternium 15, DMDM hydantoin and bronopol) at the oncentration of 0.2% were detected by acetylacetone colorimetry. They were all formaldehyde-positive. Quaternium 15 liberated 58.80% formaldehyde (1176 ppm). DMDM hydantoin released 17.12% (342 ppm). Diazolidinyl urea gave 15.43% (309 ppm). Imidazolidinyl urea gave 12.53% (251 ppm) and bronopol released only 4.40% (88 ppm). Quaternium 15 liberated the highest amount of formaldehyde, which was almost 3.43 times amount that DMDM hydantoin did. In theory, one mole of quaternium 15 produce 6 moles of formaldehyde and one mole DMDM hydantoin generate two-mole formaldehyde[17]. From acetylacetone colorimetry, we did not see the preservatives liberating formaldehyde as much as they should, based on the theory. But the preservatives, which theoretically should give more free formaldehyde, tended to liberate more. As Engehardt and Klinkner[19] pointed out, the exact formaldehyde-releasing rate of preservatives varied with different formaldehyde donors, pH values, temperature and storage time. Hurley[20] indicated some formaldehyde donors release only trace amount of formaldehyde.

III. *The Comparison of Analysis by Acetylacetone Colorimetry Method and by HPLC Method*

Engelhardt and Klinkner[19] used acetylactone as derivation reagent of formaldehyde with HPLC and post column derivation approach. Reaction of acetylactone and formaldehyde was heated for catalysis while detected by either UV or HPLC. Meanwhile, reaction of 2,4-DNPH and formaldehyde does not need to be heated. We considered using regular lab facility and suggested that derivation reaction of formaldehyde by 2,4-DNPH be performed before HPLC analysis, instead of using acetylactone as derivation reagent before UV detection.

Given five 0.2% formaldehyde donor solutions, we compared the formaldehyde percentage obtained from acetylacetone colorimetry and HPLC. It was found that measured formaldehyde of diazolidinyl urea, DMDM hydantoin and imidazolidinyl urea via acetylacetone colorimetry method was 1.62~1.90 fold more than those from HPLC while that from bronopol was 8.30 fold and that from quaternium 15 was as high as 17.35 fold (Figure 6).

Although 2,4-DNPH can react with both aldehydes and ketones, the chromatographed free formaldehyde can be detected by HPLC. 0.2% formaldehyde and 5 formaldehyde donors were detected by HPLC. The peaks with the same retention time were subject to photodiode array analysis. The spectrograms showed they were all 2,4-DNPH derivatives of formaldehyde (Figure 7).

Gryllaki-Berger *et al.*[12] believed the color given from

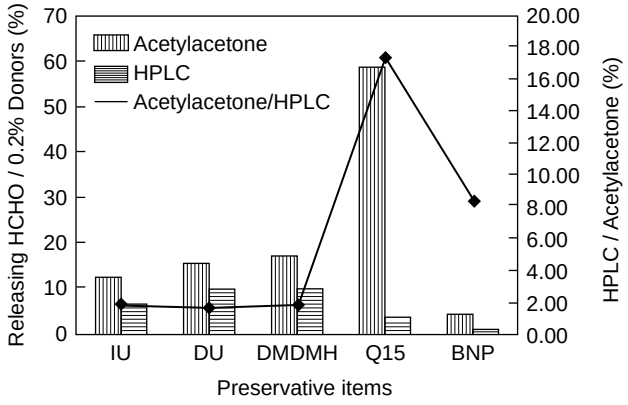

Figure 6. Comparison of the formaldehyde released from five kinds of 0.2% formaldehyde donors between acetylacetone method and HPLC method

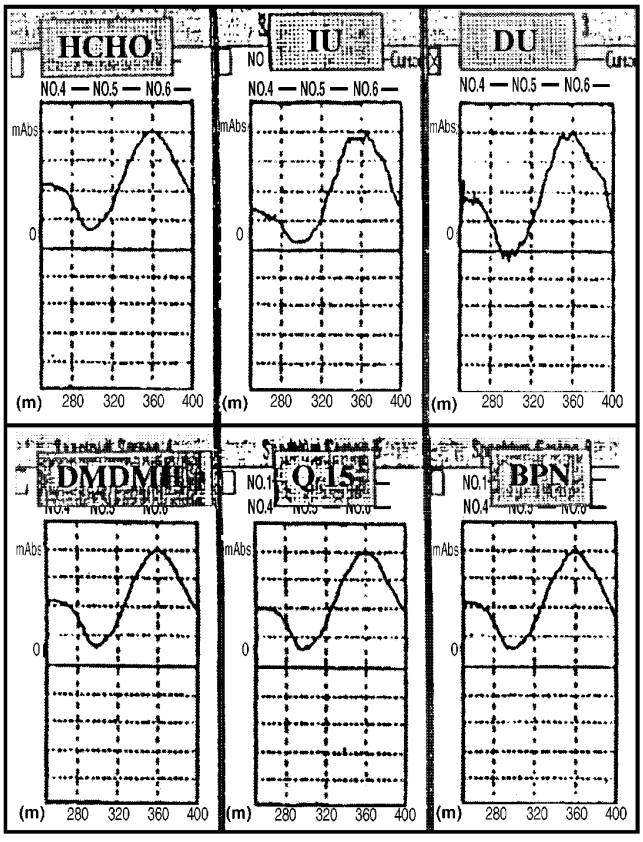

Figure 7. Spectra of formaldehyde and formaldehyde donors detected by photodiode array connected with HPLC at the same retention time (10.97 mins)

acetylacetone colorimetry would be effected by pigment in the products, salicylaldehyde or heating. It was further confirmed by our observation that formaldehyde measurement was effected largely by heating in acetylacetone colorimetry analysis. Quaternium 15 was affected the most.

By HPLC, we detected how much the five 0.2% formaldehyde donors released formaldehyde in tetrahydrofuran solutions. Diazolidinyl urea released the most formaldehyde (9.54%,191 ppm). DMDM hydantoin released 9.38% (188 ppm), imidazolidinyl urea released 6.59% (132 ppm), quaternium 15 released 3.39% (68 ppm) and bronopol released the least for only 0.53% (11 ppm). It was reported that quaternium 15 is stable only at pH 4.0 – 10.5. During the reaction in which the pH is less than 2, quaternium 15 was unstable and release more formaldehyde[21]. Less formaldehyde was released by quaternium 15 was in our HPLC analysis than that described by Benassi *et al.*[21] This might be due to the elevated pH (4.5 – 6) after derivation. More evidence should be provided for further confirmation.

Berke & Rosen[22] and Rosen & Mcfarland[23] indicated that diazolidinyl urea was affected by anionic solution, cationic solution or solution with proteins contented. In anionic samples, one mole of diazolidinyl urea can release 2.1-mole formaldehyde in 5 mins, not the theoretical 4 moles. Preservatives in anionic samples released formaldehyde from high to low as the following: quaternium 15 > diazolidinyl urea > DMDM hydantoin > imidazolidinyl urea. In our HPLC experiment, the 0.2% preservatives in tetrahydrofuran released formaldehyde: diazolidinyl urea > DMDM hydantoin > imidazolidinyl urea while quaternium 15 is lower than any of the former three. The reason might be that quaternium 15 is more stable in tetrahydrofuran and less interference in formaldehyde detection by HPLC method.

Formaldehyde donors liberated formaldehyde in different extent[19,20]. Those that partially liberated formaldehyde were called bonded formaldehyde. Those that liberated formaldehyde freely were called free formaldehyde. So the formaldehyde content from formaldehyde donors we measured in acetylacetone colorimetry method includes both free and bonded formaldehyde, or total amount of formaldehyde. Presumably, if cosmetics contain formaldehyde donors, we will get higher free formaldehyde measurement via acetylacetone colorimetry method than that by HPLC. Therefore, acetylacetone colorimetry is not good for the analysis of free formaldehyde from formaldehyde donors.

IV. *Formaldehyde Content Survey on 100 Cosmetic Merchandises*

We conducted a formaldehyde content survey on 100 cosmetic merchandises. The measured content by acetylacetone colorimetry method was considered total amount of formaldehyde, and that by HPLC was considered free formaldehyde. 53% samples had positive response for formaldehyde. Measured content by acetylacetone colorimetry was 10 – 630 ppm. Four of them exceeded the 0.05% limit which Europe Union require for the labeling. However, the measured content by HPLC was 20~165 ppm which was lower than the regulated amount of 0.2% in EU and 1000 ppm in Taiwan (Figure 8). Rastogi investigated 285 cosmetics including commercially available shampoos and creams in Denmark[24]. The result showed 29% samples contained formaldehyde 0.001% – 0.149% within which 3.5% has bonded formaldehyde higher than 0.05% and 2.8% has free formaldehyde higher than 0.05%.

Imports were collected from 32 different companies of 15 countries throughout the world including Australia, Belgium, Canada, Chile, England, France, Germany, Indonesia, Japan, Korea, Singapore, Swiss, Switzerland, Thailand, and USA. While domestics came from 21 companies.

According to Goldemberg's report[3], Japan and Thailand prohibit the usage of formaldehyde in cosmetics. No formaldehyde was found in 4 Japanese merchandises while one Thai baby body soap contained 63 ppm of formaldehyde with 25 ppm of the free formaldehyde. 3 items from the same Korean brand contain 60~230 ppm of formaldehyde. 8 out of the 18 items from 6 Europe countries had trace amount of formaldehyde around 20~400 ppm. USA and Australia did not prohibit formaldehyde-contained cosmetics. 8 out of 19 American products have formaldehyde ranging from 10 to 610 ppm with the free formaldehyde around 8~109 ppm. 5 items, which came from 3 different Australia companies, had total formaldehyde from 100 to 630 ppm. Among the items, one body soap and one cleaning lotion contained formaldehyde 550 and 630 ppm and free formaldehyde 118 and 165 ppm respectively.

Seventeen out of forty-six domestics contained formaldehyde with total amount of 10 – 620 ppm. One cream product contained formaldehyde 620 ppm with free formaldehyde 96 ppm which is lower than the 1000-ppm limit in Taiwan.

None of the 100 cosmetics was labeled formaldehyde. 2 domestics and 18 imports were labeled containing

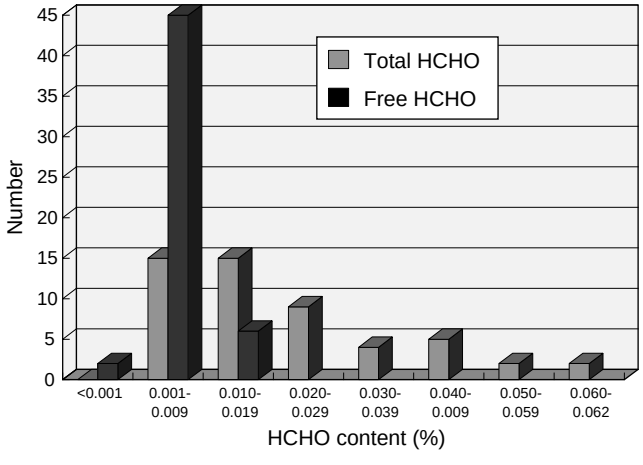

Figure 8. Distribution of formaldehyde content in cosmetic products

formaldehyde-releasing preservatives. The distributions of formaldehyde content were obtained by acetylacetone colorimetry and HPLC methods as shown in Figure 9. 8 was labeled containing imidazolidinyl urea with total amount of formaldehyde 50 – 390 ppm, free formaldehyde 7 – 79 ppm. One was labeled containing bronopol with total formaldehyde 20 ppm and free formaldehyde 5 ppm. 4 were labeled containing DMDM hydantoinwith total formaldehyde 140 – 450 ppm and free formaldehyde 8~100 ppm. Among them, one contained both DMDM hydantoin and diazolidinyl urea. 4 were labeled containing diazolidinyl urea with total formaldehyde 420 – 630 ppm and free formaldehyde 8 – 118 ppm. 4 were labeled containing quaternium 15 with total formaldehyde 60 – 370 ppm and free formaldehyde 23 – 109 ppm (Figure 9). 33 items were formaldehyde positive and did not have proper labeling of the content of either formaldehyde or formaldehyde donor. These items had total formaldehyde 10 – 620 ppm and free formaldehyde 3 – 165 ppm. EU dictate the mandatory formaldehyde-donor labeling for any having more than 0.05% formaldehyde. Overall, 4 items contained total formaldehyde more than 0.05%. But only 20 – 165 ppm free formaldehyde was measured by HPLC method which is lower than EU regulated labeling amout 0.05% and usage limit 0.2%.

Sampling products were sorted into three categories: Part I were shampoo, conditioner, body wash, facial cleanser and clear lotion, totally 50 items. Among them, 22 were detected containing formaldehyde. Part II were Emulsion, milky cream and nourishing cream, totally 41 items. Among them, 26 were detected containing formaldehyde. Part III were Lotion, astringent lotion, toner and moisturizer spray, totally 9 items. Among them, 5 were detected containing formaldehyde (Table 4). Considering the application of these cosmetics, 50 items were rinse-off samples (I), 22 of which contained formaldehyde; the other 50 were leave-on samples (II, III), and 31 of which contained formaldehyde. Two leave-on and two rinse-off items contained more than 0.05% formaldehyde over which EU requests clear labeling. 3 out of the four shampoos were imports while the other one was made domestically (which did not label the preservative content).

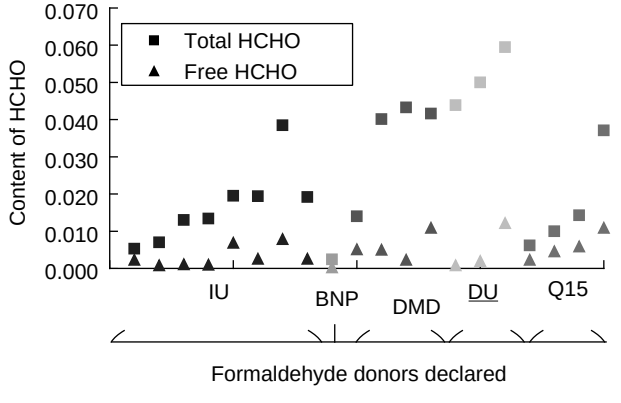

Figure 9. Distribution of formaldehyde content of samples declared formaldehyde donors

Table 4. Detection of formaldehyde in grouped samples

Type of product	HCHO (+) / sampled
I. Shampoos, hair conditioners, bubble baths, body cleaners, cream showers, etc.	22/50
II. Skin creams, body lotions, etc.	26/41
III. Skin tonics, body spray,	5/9
Sum	53/100

I: rinse-off products
II & III: leave-on products

Overall, acetylacetone colorimetry method is not good for detection of free formaldehyde, corresponding to what Summers (1990) suggested[25]. Although acetylacetone colorimetry has defects as we described, Gryllaki-Berger *et al.* (1992)[12] thought this method was still practical for rapid screen in large samples. We will keep investigating the analysis methods for various formaldehyde donors[4,5,24,25] in frequently used cosmetics.

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