Determination of four naphthalenediols in cosmetic samples by sweeping-micellar electrokinetic chromatography and a comparison with HPLC

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ABSTRACT

A sweeping micellar electrokinetic chromatography (sweeping-MEKC) method was developed for the determination of 1,7-naphthalenediol, 2,3-naphthalenediol, 1,5-naphthalenediol and 2,7-naphthalenediol in cosmetics. Several parameters affecting sweeping-MEKC method were studied systematically and the separation conditions were optimized as 20 mM NaH₂PO₄–110 mM SDS and 40% (v/v) MeOH (pH 2.4), with −22 kV applied voltage and UV detection at 230 nm. The sample matrix is 60 mmol L⁻¹ NaH₂PO₄ and sample introduction was performed at 3 psi for 6 s. Separation of the four naphthalenediols was completed in less than 17 min. Limit of detection (LOD) and limit of quantitation (LOQ) are 0.0045–0.0094 mg mL⁻¹ and 0.015–0.031 mg mL⁻¹. Linear relationship ($r^2 > 0.999$) is satisfactory at the range of 0.1–10 mg mL⁻¹. The developed method has been successfully applied to the determination of the four naphthalenediols in real cosmetic samples, with recoveries in foundation, sun cream and lotion in the range of 92.3%–106.8% and relative standard deviation (RSD) less than 4.15%. A HPLC method described in the National Standards of the People’s Republic of China was carried out for the comparison with the proposed method. The results showed that the proposed sweeping-MEKC method has the advantages of fast, low cost with comparative sensitivity.

KEYWORDS

sweeping-micellar electrokinetic capillary chromatography, naphthalenediol, cosmetic, high performance liquid chromatography

INTRODUCTION

In organic synthesis, 1,7-naphthalenediol, 2,3-naphthalenediol, 1,5-naphthalenediol and 2,7-naphthalenediol are important pharmaceutical intermediates, and the dosage must be strictly controlled [1–3]. 2,7-Naphthalenediol is a raw material for the synthesis of sulfonic acid compounds and divinyl naphthalene compounds in chemical production, while 1,5-naphthalenediol plays an important role in biochemical research [4, 5]. 1,7-Naphthalenediol and 2, 3-naphthalenediol are prohibited components in cosmetics, while the addition of 2,7-naphthalenediol and 1,5-naphthalenediol is strictly controlled [6]. Long-term excessive exposure to naphthalenediols can cause serious irritation to respiratory system and eyes, and may cause skin allergies [7, 8]. Therefore, it is necessary to establish a simple and efficient separation method to determine the content of the four naphthalenediols. The structures of the four naphthalenediols are given in Fig. 1.

High performance liquid chromatography (HPLC) is an existing method for the determination of naphthalenediols, which is considered to be a simple and feasible method for the determination of naphthalenediols [9–13]. Capillary electrophoresis (CE) is known as an
environmental friendly method with high efficiency, short separation time and low reagent consumption [14, 15]. However, the small injection volume causes poor concentration sensitivity, which limits the usefulness of CE for trace analysis. Therefore, it is an urgent problem for electrophoresis workers to improve the sensitivity of CE. The on-line enrichment technology is a method of concentrating samples in the process of separation. The most common on-line enrichment methods are field amplification [16–18], sweeping [19–21] and isokinetic electrophoresis stacking [22–24]. Sweeping, a technique used in micellar electrokinetic chromatography (MEKC), is the picking and accumulation of the analytes by the pseudo stationary phase (PSP) that penetrates the sample zone containing no PSP during application of voltage. Sweeping-MEKC has been successfully applied to many analytical fields. However, the method of determination of the four naphthalenediols in cosmetics by sweeping-MEKC has not been reported.

In this work, a sweeping-MEKC method was established for on-line enrichment and separation of 1,7-naphthalenedioli, 2,3-naphthalenedioli, 1,5-naphthalenediol and 2,7-naphthalenedioli. A comparison with a HPLC method described in the national standard of the People’s Republic of China [25] was also carried out. The results showed that the established sweeping-MEKC method has the advantages of fast, low cost with comparative sensitivity.

**EXPERIMENTAL**

**Chemicals and materials**

1,7-naphthalenedioli, 2,3-naphthalenedioli, 1,5-naphthalenedioli and 2,7-naphthalenedioli were purchased from Beijing Manhage Bio-Technology Company (Beijing, China). Foundation, sun cream and lotion were obtained from the supermarket nearby. Methanol and phosphoric acid were of chromatographic grade and were purchased from Kemel Chemical Reagent Co., Ltd (Tianjin, China). Acetic acid and 95% ethanol were purchased from Northern Tianyi Chemical Reagent Factory (Tianjin, China) and Yongda Chemical Reagent Co., Ltd. (Tianjin, China). Disodium hydrogen phosphate (NaH$_2$PO$_4.2H_2$O, ≥ 99.0%) and sodium hydroxide (NaOH) were of analytical grade and were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Sodium dodecyl sulfate (SDS) was purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China).

The standard stock solutions were prepared by dissolving the four naphthalenediols in MeOH respectively with the concentration of 100 μg ml$^{-1}$. They were stored in a refrigerator at 4°C. 0.5 g (accurate to 0.001 g) foundation, sun cream and lotion samples were added in a 10 ml plug colorimetric tube respectively. 4 ml MeOH were added to the samples and mixed well on a vortex oscillator. Then kept in an ultrasonic bath for 15 min. After the temperature of solution reached room temperature MeOH were added to fix the volume to 5 ml. 2 ml sample solution were taken in a centrifuge tube and centrifuged at 6,996 x g for 2 min. After centrifugation, 1 ml sample was blown dry with nitrogen and reconstituted with 1 ml 60 mM NaH$_2$PO$_4$. Finally, the samples were filtered through microporous nylon filters with a pore size of 0.22 μm prior to use.

**Apparatus**

The SCIEX P/ACE™ MDQ plus CE system (Fullerton, CA) equipped with a diode array detector (DAD) and a fused silica capillary (Yongnian Photoconductive Fiber Factory, Hebei, China), with an i.d. of 75 μm and an o.d. of 375 μm were used. The total length of the capillary was 50.2 cm and the effective length was 40 cm. The HPLC system consisted of a Waters e2695 pump, a Waters 2998 PDA detector and an Empower chromatography management system (Waters, Milford Massachusetts, USA). A C18 reverse phase column (Tianyuan Technology Co., Ltd., Tianjin, China; Aces aqC18, 5 μm, 250 x 4.6 mm) was used. Data acquisition was performed using Karat 32 software (Beckman-Coulter, Fullerton, CA, USA).

**Sweeping-MEKC conditions**

Before the first use, new capillaries were conditioned with 1 mol L$^{-1}$ NaOH for 20 min, Milli-Q water for 15 min and buffer for 30 min. At the beginning of every day, the capillary was washed with 1 mol L$^{-1}$ NaOH, water and running buffer for 5 min, 5 min and 10 min, respectively. The detection wavelength of was set at 230 nm, and the temperature of the capillary was maintained at 25°C. All solutions were filtered through microporous nylon filters with a pore size of 0.22 μm prior to use. Between runs, the capillary was rinsed with running buffer for 5 min. Samples were injected at a pressure of 3 psi (1 psi = 6,894.76 Pa) for 6 s. Working stock solutions were diluted with a sample matrix of 60 mM NaH$_2$PO$_4$ without SDS. The running buffer was composed of 20 mM NaH$_2$PO$_4$, 110 mM SDS and 40% (v/v) MeOH (pH 2.4). In this work, acidic buffer solution with low pH was used, so that the electroosmotic flow (EOF) could be ignored. During the separation, a reverse voltage of −22 kV was applied (negative injection). As the PSP, SDS micelles with negative charge move toward the positive electrode (detection window), whose electrophoretic speed is faster than that of the uncharged naphthalenediols. During the application of voltage, the PSP in background electrolyte solution (BGE) penetrates the sample region and the sample band of the analyte narrows.

To estimate the sensitivity increase achieved by using the sweeping-MEKC method, sensitivity enhancement factors...
(EF) based on peak area were estimated from the following equation:

$$EF = \frac{A_{\text{swept}}}{A_{\text{MEKC}}}$$  \hspace{1cm} (1)

where $A_{\text{swept}}$ and $A_{\text{MEKC}}$ are the peak areas of the analytes after sweeping-MEKC and conventional MEKC in which separation conditions were optimized as 20 mM Na$_2$B$_4$O$_7$, 50 mM SDS, pH 9.8, with 22 kV applied voltage, UV detection at 230 nm, and samples were injected at a pressure of 0.5 psi for 5 s.

**HPLC conditions**

The mobile phase was composed of methanol and 0.1% acetic acid solution for gradient elution with a 25–55% linear gradient of methanol from 0 to 35 min at a flow rate of 1.0 mL min$^{-1}$ according to the National Standards of the People’s Republic of China (GB/T 35829-2018) [25]. All analyses were performed at room temperature with the PDA detection wavelength of 230 nm. The samples were prepared in the same manner as for MEKC analysis except for reconstitution with 60 mM Na$_2$HPO$_4$. MeOH solvent was used for samples instead of matrix solution. The volume of every sample injected into the column was 10 µL.

**RESULTS AND DISCUSSION**

**Optimization of sweeping-MEKC separation conditions**

Optimization of sample injection time. For sweeping-MEKC, the injected length of the sample zone is restricted by the value of $1/(1+k)$, where $k$ is the capacity factor of the analyte. Only the column length restricts the length of injection when $k$ goes to infinity. The sample length of injection is suggested to be optimized when the $k$ value of the analyte is not high [26]. In this work, 110 mmol L$^{-1}$ SDS, 20 mmol L$^{-1}$ Na$_2$HPO$_4$ (pH 2.4) containing 35% MeOH were used as buffer solution and the sample matrix was 60 mmol L$^{-1}$ Na$_2$HPO$_4$. The sample solution was injected at 3 psi for 6, 8 and 10 s into the column. From Fig. 2, we can see that the peak areas of the analytes increased with the increase of sample injection time. However, the peak of the four naphthalenediols split when the sample injection time increased to 8 and 10 s. The reason is that the sweeping performance is influenced by injected sample volume, and with the increasing of sample injection time, the PSP is not sufficient enough to sweep all the analytes and the peaks split. At 6 s, the peak shape and the resolution of the four naphthalenediols is relatively satisfactory. Therefore, we chose 6 s as the best injection time at 3 psi.

Optimization of organic modifier. The addition of organic modifier can impact the distribution of the analytes between micelles and buffer solution, which can improve the separation degree and peak shape of the analytes. It can also increase the solubility of the analytes. In this work MeOH was used as organic modifier and the effect of the content of MeOH in the range of 30%–45% on the separation and enrichment of the four naphthalenediols was investigated. As shown in Fig. 3, baseline separations were obtained under the four MeOH levels. However, the last peak (1,5-naphthalenediyl) has obvious shoulder in front when the content of MeOH were 30% and 35%. In addition, with the increase of MeOH content, the migration times of the four naphthalenediols prolonged. Given full consideration of the peak shape and separation time, 40% MeOH was chosen.

Optimization of the concentration of SDS. The analyte with higher retention factor has better sweeping efficiency, while one of the factors affecting the retention factor is the concentration of PSP in BGE. To investigate the influence of
SDS concentration on separation, experiments were carried out using 20 mM NaH2PO4 containing 40% MeOH at pH 2.4 with different concentrations of SDS (80−120 mM). As shown in Fig. 4, with the increase of SDS concentration, the migration time of analytes decreased slightly because more and more of the analytes were incorporated into the micellar phase. Considering the migration time, peak shape and peak area, 110 mM SDS was used.

Optimization of the running buffer concentration and sample matrix composition. Generally, phosphate solutions are used as buffer solutions with low pH. The effect of the concentration of running buffer on the separation of the four naphthalenediols in the range of 10−40 mM is illustrated in Fig. 5 (A). We can see that changing the concentration of NaH2PO4 has little effect on the migration time of the four naphthalenediols. The sensitivity and peak area of the analytes are the highest at 20 mM NaH2PO4. Therefore, 20 mM NaH2PO4 was chosen. Since the sample matrix could affect the degree of sample stacking, we need to investigate the concentration of it. The sample matrix is composed of NaH2PO4 solution without SDS and the effect of the concentrations from 40 to 100 mM on sweeping was investigated. The results in Fig. 5 (B) indicated that the highest peak intensity of naphthalenediols was achieved using 60 mM NaH2PO4 as the sample matrix solution.

Optimization of separation voltage. Separation voltage is also a very important parameter in sweeping-MEKC. Usually higher voltage is needed to make sweeping-MEKC fast and efficient. The effect of different voltages (−20, −22, −24 and −26 kV) on the separation of the analytes was investigated by using a running buffer consisting of 20 mM NaH2PO4, 110 mM SDS and 40% MeOH at pH 2.4. As shown in Fig. 6, with the increase of voltage the migration time of the analytes became shorter gradually. When the applied voltage was higher than −22 kV the last peak (1,5-naphthalenediol) had obvious shoulder in front. So −22 kV was used.

To sum up, the optimum conditions are as follows: BGE composed of 20 mM NaH2PO4, 110 mM SDS, and 40% MeOH (pH=2.4); sample matrix composed of 60 mM NaH2PO4; sample was injected by pressure injection at 3 psi for 6 s. The corresponding electropherogram of 1,7-naphthalenediol, 2,3-naphthalenediol, 1,5-naphthalenediol and 2,7-naphthalenediol mixed standard solution obtained under the optimized conditions is shown in Fig. 7 (A). The retention time of 2,3-naphthalenediol, 1,7-naphthalenediol, 2,7-naphthalenediol and 1,5-naphthalenediol is 12.10 min, 13.56 min, 15.27 min and 16.68 min, respectively.

**HPLC method**

The four naphthalenediols were analyzed by the HPLC method as described in the National Standard of the People’s...
The retention time of 1,5-naphthalenediol, 2,7-naphthalenediol, 1,7-naphthalenediol and 2,3-naphthalenediol is 16.33 min, 20.30 min, 25.64 min and 28.09 min respectively. From Fig. 7, we can see that the separation time of the four analytes by using the HPLC method is longer than that with the sweeping-MEKC method.

Validation of Sweeping-MEKC and HPLC methods

To verify both the sweeping-MEKC and HPLC methods, system suitability, linearity, LOD, LOQ, EF and precision were extensively validated.

System suitability. The values of migration/retention time \((t)\), tailing factor \((T)\) and theoretical plates \((N)\) were evaluated by using six replicate injections of a same mixed standard solution of the analytes. The results obtained are listed in Table 1.

Linearity, LOD, LOQ and EF. The results obtained are summarized in Table 2. The EFs of 2,3-naphthalenediol, 1,7-naphthalenediol, 2,7-naphthalenediol and 1,5-naphthalenediol are 32, 29, 56 and 42, respectively. From Table 2 we can conclude that there is good \((r^2 > 0.999)\) linear correlations between the concentration of the four naphthalenediols and the corresponding peak areas by both sweeping-MEKC and HPLC methods. The limit of detection (LOD) and the limit of quantitation (LOQ) were obtained as

| Table 1. Results of system suitability tests for analysis of the four naphthalenediols \((n = 6)\)ab |
|---|---|---|---|
| Method | Analytes | Migration/retention time, (min) | Tailing factor | Theoretical plate number |
| sweeping-MEKC | 1,7-naphthalenediol | 13.56 ± 0.16 | 0.94 ± 0.03 | 70809 |
| | 2,3-naphthalenediol | 12.10 ± 0.15 | 0.94 ± 0.02 | 97129 |
| | 1,5-naphthalenediol | 16.68 ± 0.16 | 0.93 ± 0.02 | 38534 |
| | 2,7-naphthalenediol | 15.27 ± 0.14 | 0.91 ± 0.04 | 54716 |
| HPLC | 1,7-naphthalenediol | 26.64 ± 0.16 | 1.06 ± 0.03 | 32382 |
| | 2,3-naphthalenediol | 28.09 ± 0.14 | 0.90 ± 0.02 | 7706 |
| | 1,5-naphthalenediol | 16.33 ± 0.12 | 1.06 ± 0.02 | 12261 |
| | 2,7-naphthalenediol | 20.30 ± 0.084 | 1.07 ± 0.04 | 16612 |

a Values are means of six measurements ± SD.
b Concentration of 5 µg/mL for the four naphthalenediols was chosen for the assays of system suitability.
Method Analytes Calibration curve $y$ Correlation coefficient $r^2$ Linear range (µg mL$^{-1}$) LOD (µg mL$^{-1}$) LOQ (µg mL$^{-1}$) EF
sweeping-MEKC 1,7-naphthalenediol $y = 39363x + 1027.5$ 0.999 0.1–10 0.0075 0.025 29
2,3-naphthalenediol $y = 62514x - 3538.2$ 0.999 0.1–10 0.0045 0.015 32
1,5-naphthalenediol $y = 65990x - 2027.5$ 0.999 0.1–10 0.0094 0.031 42
2,7-naphthalenediol $y = 65578x - 304.96$ 0.999 0.1–10 0.0069 0.023 56

HPLC 1,7-naphthalenediol $y = 130285x + 12904$ 0.999 0.75–20 0.018 0.060 -
2,3-naphthalenediol $y = 264155x + 7553$ 0.999 0.75–20 0.0098 0.033 -
1,5-naphthalenediol $y = 166698x + 11155$ 0.999 0.75–20 0.012 0.040 -
2,7-naphthalenediol $y = 206908x + 40328$ 0.999 0.75–20 0.0085 0.028 -

$^a$ y and x stand for the peak area and the concentration (µg mL$^{-1}$) of the four naphthalenediols, respectively.

three and ten times of the signal-to-noise ratio (S/N) respectively. The LODs obtained by sweeping-MEKC method were 0.0045–0.0094 µg mL$^{-1}$ and 0.0085–0.018 µg mL$^{-1}$ by HPLC method. The LOQs obtained were 0.015–0.031 µg mL$^{-1}$ by sweeping-MEKC method and 0.028–0.060 µg mL$^{-1}$ by HPLC method.

Intra-day precision and inter-day precision. The intra-day precision and inter-day precision were obtained by injecting the same mixed standard solution for 6 times on one day and 6 consecutive days respectively. The relative standard deviations (RSDs) were calculated for both the migration/retention time and the peak area of the four analytes for evaluation, and the results were satisfactory. The results are listed in Table 3.

Sample analysis

Under the optimized conditions, three different kinds of cosmetic samples i.e. foundation, sun cream and lotion (marked as A, B and C) were analyzed by both sweeping-MEKC and HPLC methods. Typical electropherograms and chromatograms of all the cosmetic samples are shown in Fig. 8. From Fig. 8 we can see that no naphthalenediols in the blank samples of the three cosmetics were detected by both two methods. As mentioned in the introduction, 1,7-naphthalenediol and 2,3-naphthalenediol are prohibited components in cosmetics and the addition of 1,5-naphthalenediol and 2,7-naphthalenediol are strictly limited. That’s why there is no signal response of the four naphthalenediols. To further evaluate the performance of the proposed method in complex matrices and verify the accuracy of both two methods, standards of the four naphthalenediols at concentrations of 0.5 µg mL$^{-1}$ and 1.0 µg mL$^{-1}$ were added to the real cosmetic samples. The recoveries of them obtained were 92.3%–106.8% by sweeping-MEKC method and 90.4%–107.5% by HPLC method. The results are listed in Table 4.

Comparison of MEKC and HPLC methods

Based on the results given above we can see that both methods can be successfully applied to the determination of the content of the four naphthalenediols in cosmetics. Combined with the on-line concentration sweeping strategy, the MEKC method can achieve even lower LODs and LOQs than those of the HPLC method. Furthermore, the developed sweeping-MEKC method has the advantages of lower reagent consumption, faster separation speed, and higher theoretical plate number, which can be potentially considered as an alternative to the existing HPLC methods in cosmetic naphthalenediol analysis.

Table 3. Precision for analysis of the four naphthalenediols by sweeping-MEKC and HPLC ($n = 6$)$^a$

| Method       | Analytes            | Migration/retention time (min) | Peak area (mAU) | Migration/retention time (min) | Peak area (mAU) |
|--------------|---------------------|-------------------------------|----------------|-------------------------------|----------------|
| sweeping-MEKC| 1,7-naphthalenediol | 1.18                          | 0.82            | 2.13                          | 3.05           |
|              | 2,3-naphthalenediol | 1.24                          | 1.06            | 1.76                          | 2.84           |
|              | 1,5-naphthalenediol | 1.08                          | 1.25            | 1.97                          | 2.65           |
|              | 2,7-naphthalenediol | 0.92                          | 1.08            | 2.38                          | 3.73           |
| HPLC         | 1,7-naphthalenediol | 0.60                          | 0.92            | 1.32                          | 2.31           |
|              | 2,3-naphthalenediol | 0.49                          | 0.85            | 1.54                          | 2.24           |
|              | 1,5-naphthalenediol | 0.73                          | 0.72            | 1.65                          | 2.56           |
|              | 2,7-naphthalenediol | 0.41                          | 0.87            | 1.27                          | 2.18           |

$^a$ Concentration of 5 µg mL$^{-1}$ individual for the four naphthalenediols was chosen for the assays of system suitability.
In this work, an efficient sweeping-MEKC method for the analysis of 1,7-naphthalenediol, 2,3-naphthalenediol, 1,5-naphthalenediol and 2,7-naphthalenediol has been developed and verified. The four naphthalenols in cosmetics could be determined within shorter separation time with comparable sensitivity compared with the HPLC method.

CONCLUSION

Fig. 8. Electropherograms (A1, B1, C1) of three samples: none-spiked (a), spiked with 0.5 μg·mL⁻¹ (b), spiked with 1.0 μg·mL⁻¹ (c); and chromatograms (A2, B2, C2) of three samples: none-spiked (a), spiked with 0.5 μg·mL⁻¹ (b), spiked with 1.0 μg·mL⁻¹ (c); Peak: (1) 2,3-naphthalenediol (2) 1,7-naphthalenediol (3) 2,7-naphthalenediol (4) 1,5-naphthalenediol (A1, A2) foundation, (B1, B2) sun cream, (C1, C2) lotion, other conditions are same as those in Figure 7.
The present study shows that sweeping-MEKC is a powerful analytical tool for rapid screening of the four naphthalenediols in cosmetics.

Conflict of interest: The authors have no conflict of interest to declare.

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| Table 4. The recoveries of the four naphthalenediols in three samples by sweeping-MEKC and HPLC methods (n = 3) |
|---------|----------|------------|-------------|-------|-----|-----|
| Method  | Sample   | Analytes   | Original amount (μg·mL⁻¹) | Added (μg·mL⁻¹) | Found ± SD (μg·mL⁻¹) | Recovery (%) | RSD (%) |
|---------|----------|------------|---------------------------|-----------------|----------------------|--------------|--------|
| sweeping-MEKC | Foundation | 1,7-naphthalenediol | –a | 0.5 | 0.49 ± 0.016 | 97.7 | 3.21 |
|          |          | 2,3-naphthalenediol | – | 1.0 | 0.98 ± 0.025 | 98.2 | 2.56 |
|          |          | 1,5-naphthalenediol | – | 0.5 | 0.48 ± 0.008 | 95 | 1.67 |
|          |          | 2,7-naphthalenediol | – | 1.0 | 1.02 ± 0.023 | 101.3 | 2.31 |
|          | Sun cream | 1,7-naphthalenediol | – | 0.5 | 0.52 ± 0.011 | 104.2 | 2.12 |
|          |          | 2,3-naphthalenediol | – | 1.0 | 0.94 ± 0.034 | 94.1 | 3.58 |
|          |          | 1,5-naphthalenediol | – | 0.5 | 0.46 ± 0.019 | 92.3 | 4.15 |
|          |          | 2,7-naphthalenediol | – | 1.0 | 1.05 ± 0.041 | 105.0 | 3.98 |
|          | Lotion   | 1,7-naphthalenediol | – | 0.5 | 0.97 ± 0.037 | 96.7 | 3.84 |
|          |          | 2,3-naphthalenediol | – | 1.0 | 1.09 ± 0.021 | 93.2 | 2.25 |
|          |          | 1,5-naphthalenediol | – | 0.5 | 0.48 ± 0.020 | 98.7 | 4.02 |
|          |          | 2,7-naphthalenediol | – | 1.0 | 0.98 ± 0.029 | 97.5 | 2.92 |
|          | HPLC     | Foundation | 1,7-naphthalenediol | – | 0.5 | 0.49 ± 0.013 | 98.3 | 2.73 |
|          |          | 2,3-naphthalenediol | – | 1.0 | 0.95 ± 0.025 | 94.6 | 2.62 |
|          |          | 1,5-naphthalenediol | – | 0.5 | 0.52 ± 0.011 | 102.3 | 2.04 |
|          |          | 2,7-naphthalenediol | – | 1.0 | 1.06 ± 0.021 | 106.0 | 1.97 |
|          | Sun cream | 1,7-naphthalenediol | – | 0.5 | 0.52 ± 0.017 | 96.4 | 3.57 |
|          |          | 2,3-naphthalenediol | – | 1.0 | 0.98 ± 0.040 | 98.5 | 4.13 |
|          |          | 1,5-naphthalenediol | – | 0.5 | 0.53 ± 0.029 | 105.6 | 3.78 |
|          |          | 2,7-naphthalenediol | – | 1.0 | 0.92 ± 0.020 | 92.3 | 2.19 |
|          | Lotion   | 1,7-naphthalenediol | – | 0.5 | 0.47 ± 0.0042 | 94.0 | 0.89 |
|          |          | 2,3-naphthalenediol | – | 1.0 | 1.04 ± 0.0094 | 104.3 | 0.90 |
|          |          | 1,5-naphthalenediol | – | 0.5 | 0.53 ± 0.0096 | 106.2 | 1.81 |
|          |          | 2,7-naphthalenediol | – | 1.0 | 1.05 ± 0.012 | 105.4 | 1.14 |
|          | HPLC     | Foundation | 1,7-naphthalenediol | – | 0.5 | 0.53 ± 0.0074 | 90.4 | 1.04 |
|          |          | 2,3-naphthalenediol | – | 1.0 | 0.93 ± 0.0074 | 92.8 | 0.80 |
|          |          | 1,5-naphthalenediol | – | 0.5 | 0.45 ± 0.0047 | 96.0 | 0.88 |
|          |          | 2,7-naphthalenediol | – | 1.0 | 0.96 ± 0.012 | 95.9 | 1.25 |
|          | Sun cream | 1,7-naphthalenediol | – | 0.5 | 0.52 ± 0.0022 | 103.5 | 0.42 |
|          |          | 2,3-naphthalenediol | – | 1.0 | 0.95 ± 0.0082 | 94.6 | 0.86 |
|          |          | 1,5-naphthalenediol | – | 0.5 | 0.52 ± 0.0045 | 103.7 | 0.87 |
|          |          | 2,7-naphthalenediol | – | 1.0 | 0.95 ± 0.014 | 95.2 | 1.47 |
|          | Lotion   | 1,7-naphthalenediol | – | 0.5 | 0.53 ± 0.0062 | 105.8 | 1.17 |
|          |          | 2,3-naphthalenediol | – | 1.0 | 1.07 ± 0.0075 | 106.7 | 0.70 |
|          |          | 1,5-naphthalenediol | – | 0.5 | 0.54 ± 0.0043 | 107.5 | 0.80 |
|          |          | 2,7-naphthalenediol | – | 1.0 | 0.94 ± 0.0082 | 94.4 | 0.87 |
|          |          | 1,5-naphthalenediol | – | 0.5 | 0.46 ± 0.00074 | 91.7 | 1.61 |
|          |          | 2,7-naphthalenediol | – | 1.0 | 1.04 ± 0.012 | 103.8 | 1.15 |
|          |          | 2,3-naphthalenediol | – | 0.5 | 0.47 ± 0.0044 | 94.2 | 0.94 |
|          |          | 1,5-naphthalenediol | – | 1.0 | 0.96 ± 0.0072 | 95.8 | 0.75 |
|          |          | 2,7-naphthalenediol | – | 0.5 | 0.47 ± 0.0054 | 94.1 | 1.15 |

*a* Not detected.
