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Quantitative determination of butylated hydroxyanisole and n-propyl gallate in cosmetics using three-dimensional fluorescence coupled with second-order calibration

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ABSTRACT

This work presents a novel approach for simultaneous determination of butylated hydroxyanisole (BHA) and propyl gallate (PG) in a very interfering environment by combining the sensitivity of molecular fluorescence and the selectivity of the second-order calibration method. The excitation–emission fluorescence matrix data are processed by applying the second-order calibration method based on the self-weighted alternating normalized residue fitting (SWANRF) algorithm. The limits of detection (LOD) were 1.2–1.3 ng/ml for BHA and 2.2–2.9 ng/ml for PG. The recoveries from spiked cosmetics samples are in the ranges 95.7–103.9% for BHA and 95.9–105.7% for PG. The proposed method avoids preconcentration and elution procedures, so it considerably decreases the analytical time and the experimental expenses. Because the instrument involved in the measurement is nonsophisticated, the experiments could be carried out in routine laboratories. Then it is compared with the HPLC method in dosage of cosmetics and organic reagents, runtime, cost per analysis and LOD.

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1. Introduction

Cosmetics are commercially available products that can not only improve the appearance of the skin but also benefit to the health of the skin because of their antioxygenation. One of the most effective ingredients of cosmetics is the antioxidant. Antioxidant can interrupt the radical-chain processes, help the skin to repair systems, help cell rejuvenation and prevent skin-cancer [1]. Therefore, plenty of synthetic phenolic antioxidants such as butylated hydroxyanisole (BHA) and propyl gallate (PG) are employed to the skin care products [2]. However, the use of these additives is not without their problems. Results of scientific studies have indicated that PG is toxic to hepatocytes and the acute cytotoxicity may be due to mitochondrial dysfunction [3], moreover, PG suppresses the growth of microorganisms by inhibiting respiration and nucleic acid synthesis [4], inhibits hepatic microsomal hydrolase and demethylase activities [5]. Reports also have demonstrated that BHA have been suspected of being responsible for liver damage and carcinogenesis in laboratory animals, and a potential link between BHA and cancer have been found [6]. Therefore, the consumption of these additives are controversial since the extensive use of such materials may result in a potential health risk.

The quantitative determination of synthetic phenolic antioxidants is of great interest, particularly since their use is subject to regulations in most countries, which define and limit the types and amounts of compounds allowed in particular cosmetics [7]. BHA and PG are innocuous additives at concentrations no higher than 0.02% of the cosmetics specimen content [7–9].

When BHA and PG are measured in cosmetics samples, the first problem to be faced is the low concentration levels present and the usual mixture of antioxidants which, due to synergism, display similar chemical properties and thus lead to mutual interference. A second problem is that cosmetic samples are very complex, usually containing many ingredients [10]. The specificity of a method is usually attained through procedures such as solubilization, purification and/or preconcentration followed by either high-performance liquid chromatography (HPLC) or liquid chromatography-mass spectrometry (LC/MS). Various approaches [1,7,8,11–15] have been used to quantify antioxidant mixtures in cosmetics. However, some of the methods require laborious sample preparation and derivatization (either pre- or post-column) must be employed, in most cases, to increase sensitivity and/or improve separation.

Fluorescence spectroscopy is fast, nondestructive and sensitive. It can give valuable information about chemical and physical properties, and has a potential for on-line industrial quality

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control. The conventional fluorescence data analysis method is often linear regression using a single wavelength, which requires a prerequisite extraction, chromatography or other sample separation steps prior to the fluorescence measurement and does not yield sufficiently detailed spectra suitable for complex sample characterization. Nevertheless, excitation–emission fluorescence matrix (EEM), also known as fluorescence landscapes, are obtained when emission spectra are measured at several excitation wavelengths. The triparametric EEM data incorporates information on excitation wavelength, emission wavelength and fluorescence intensity. With EEM, the spectral information content is increased, making it easier to accurately characterize multicomponent samples [16]. However, the EEM data are nonselective when measured on complex samples. The recorded signals are made up of the signal from all of the contributing fluorophores. Thus, the fluorescence for one sample consists of a number of overlapping signals.

An up-to-date approach to improve the selectivity of analytical methods is the use of advanced chemometrics tools, such as second-order calibration methods. Some second-order calibration methods allow information on concentrations and spectral profiles of sample components to be extracted directly even in presence of uncalibrated interferences [17–24]. This property, named "second-order advantage" [25,26], avoids the major obstacle of univariate and first-order analytical methods applied to complex mixtures. Many examples of second-order advantage applied to complex matrices were recently reported [18–24,27], which detected some analytes of interest even in the presence of uncalibrated interferences through the three-dimensional excitation–emission fluorescence matrix (EEM) coupled with the second-order calibration method.

However, although BHA, PG and most phenolic antioxidants were found to posses strong native fluorescence (Fig. 1a, b) which means a lower limit of detection can be obtained, HPLC–UV method is the most widely used method for the simultaneous quantification of phenolic antioxidants. To the best of our knowledge, up to now, fluorescence detectors are only used for determination of ethoxyquin [28–30], BHA, BHT and TBHQ [31]. Interestingly, it should also be noted that, so far, little literature concerned the fluorescence spectroscopy method for determination of phenolic antioxidants.

Therefore, in this paper, a novel method, EEM combined with the second-order calibration method based on the self-weighted alternating normalized residue fitting (SWANRF) algorithm [32], is proposed for the direct quantitative analysis of butylated hydroxyanisole (BHA) and propyl gallate (PG) in cosmetics samples. In order to assess the usefulness of the proposed strategy, it is validated and compared with the modified HPLC based on the AOAC official method 983.15 (1994). Remarkable differences between them are shown and discussed, which illustrated the advantages of the new approach, such as smaller dosage of cosmetics, shorter runtime, lower cost per analysis and lower limit of detection.

2. Theory

2.1. Trilinear component model for second-order calibration

When a sample produces a $I \times J$ data matrix, such as an EEM (here, I is the number of excitation wavelengths, J is the number of emission wavelengths), the corresponding data can be stacked to compose a cube. The size of such a cube is $I \times J \times K$ (K is the number of samples). Since EEM follow a trilinear component model, the responsive data cube $\underline{\mathbf{X}}$ can be written as:

$$x_{ijk} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} + e_{ijk} \quad (i = 1, 2, ..., I; \quad j = 1, 2, ..., J; \quad k = 1, 2, ..., K) \tag{1}$$

where N denotes the number of factors, which are the total number of detectable components, including the analytes and the background as well as uncalibrated interferences. x_{ijk} is the fluorescent intensity of sample k at excitation wavelength i and emission wavelength j. a_{in}, b_{jn}, and c_{kn} are the typical elements of $\mathbf{A}$ ($I \times N$), $\mathbf{B}$ ($J \times N$) and $\mathbf{C}$ ($K \times N$), respectively. e_{ijk} represents the element of $\underline{\mathbf{E}}$ which is residual error term of the same dimensions as $\underline{\mathbf{X}}$.

2.2. SWANRF algorithm

Self-weighted alternating normalized residue fitting (SWANRF) algorithm for trilinear decomposition of a three-way data arrays partially reextract valid information from the residue and further remove invalid information to the residue based on the truncated least squares method [32]. It can deal with higher collinearity problems and achieve very smooth profiles at high noise level. We can see from Fig. 1(a, b) and Fig. 2(a-B, b-B), our data have the problem of high collinearity and noise level. Therefore, SWANRF was selected for trilinear decomposition of this three-way data. The concrete theory and the model of second-order calibration method based on SWANRF algorithm (SWANRF method) have had been discussed in details in the relevant references [32], so it is not described here.

2.3. Figures of merit

Figures of merit (FOM) are regularly employed for method comparison. The limit of detection (LOD) [33] of one method is the lowest quantity of a substance that can be distinguished from the absence of that substance (a background value) within a stated confidence limit. The limit of quantification (LOQ) [34] is the limit at which we can reasonably tell the difference between two different values. Those FOM are estimated as

$$SEN = \lambda\{[(\mathbf{A}^T A)^{-1}] \times [(\mathbf{B}^T B)^{-1}]\}_{nn}^{-1/2} \tag{5}$$

$$LOD = 3.3s(0) \tag{6}$$

$$LOQ = 10 \times s(0) \tag{7}$$

where nn means the (n, n) element of matrix $[(\mathbf{A}^T\mathbf{A})^{-1} \times (\mathbf{B}^T\mathbf{B})^{-1}]$, λ is the total signal for component n at unit concentration, and the symbol * indicates the Hadamard product. $s(0)$ is the standard deviation in the predicted concentration for three different background blank samples, in the SWANRF.

2.4. Software

All calculations were done in Matlab environment and run on a personal computer E4600 processor with 1 GB RAM under Windows XP operating system. A routine for SWANRF was written in our laboratory following a previously known second-order calibration algorithm.

3. Experimental

3.1. Cosmetics specimens

The cosmetics were purchased in supermarket (Changsha). For cosmetics specimens, namely latex and emulsion, a pleasant amount (6.74–7.38 mg for fluorescence and 400–440 mg for HPLC) was weighted and dissolved in methanol, diluting to 9 ml with methanol in 10 ml centrifuge tube. Next it should be ultrasonically treated for 10 min and then centrifuged at 10,000 r min^{-1} for 10 min.

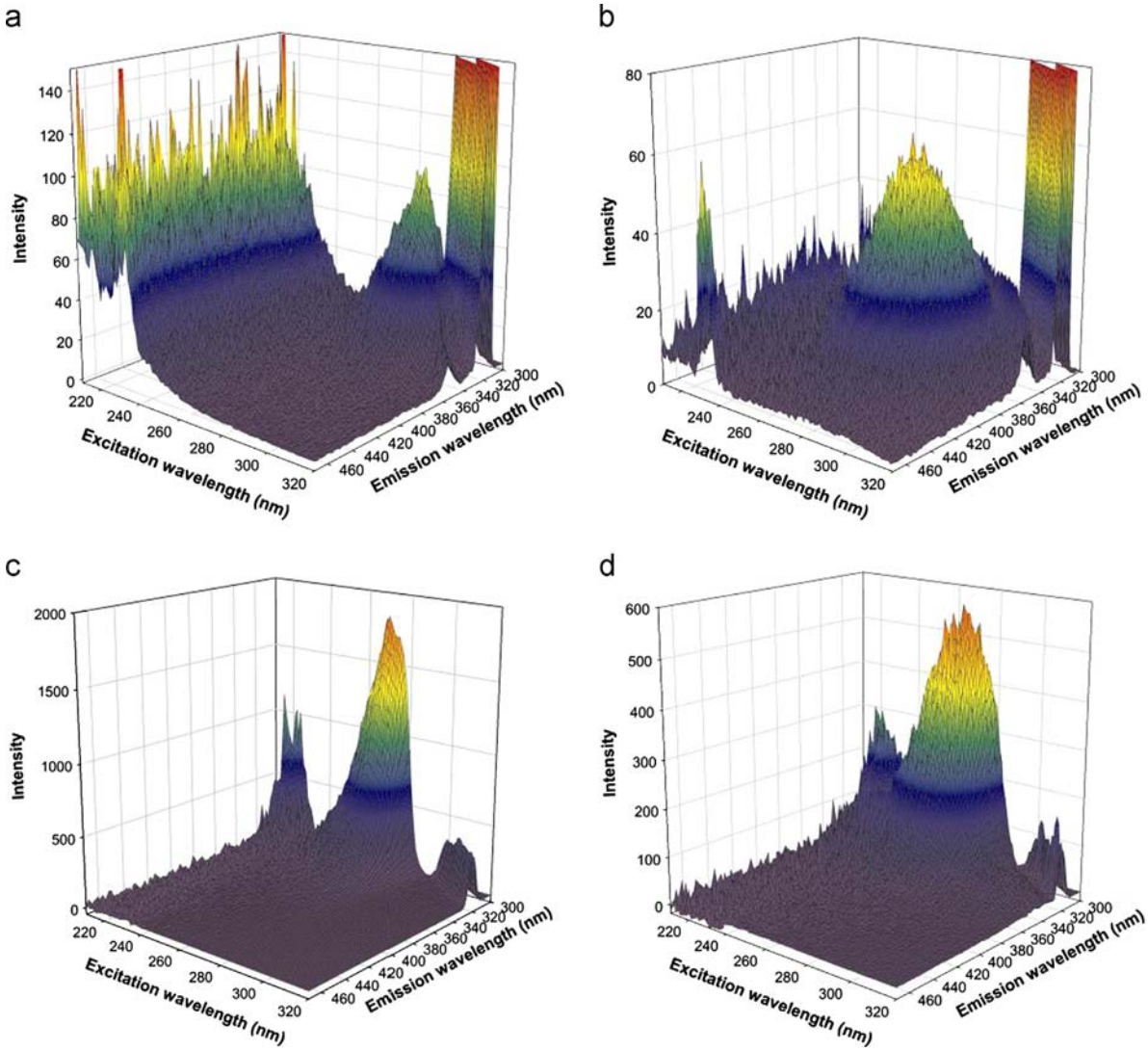

Fig. 1. Three-dimensional plots of the excitation–emission matrix fluorescence: (a) 0.0746 μg/ml of pure butylated hydroxyanisole (BHA); (b) 0.2196 μg/ml of pure propyl gallate (PG); (c) 7.35 mg of latex and (d) 7.34 mg of emulsion, diluting to 9 ml with methanol.

3.2. Reagents and chemicals

Butylated hydroxyanisole (BHA) and propyl gallate (PG) were purchased from Aladdin (Shanghai, China). Methanol and acetonitrile were obtained from Merck (Tedia, USA). Formic acid was purchased from Adamas Reagent Company. All reagents were of high-purity grade and used as received.

Stock solutions of BHA and PG of 200 μg/ml were prepared in methanol. Those solutions were spectrophotometrically stable when protected from light and kept in the refrigerator at 5 °C for a maximum of 2 weeks. From these solutions, more diluted methanol solutions (fluorescence: 0.06–0.12 μg/ml for BHA and 0.09–0.22 μg/ml for PG, HPLC: 8.31–29.10 μg/ml for BHA and 8.36–33.40 μg/ml for PG) were obtained, which were prepared immediately before use. Note that all solutions were filtered through 0.45 μm nylon filters before use in HPLC.

3.3. Excitation–emission fluorescence matrix coupled with second-order calibration method analysis

Excitation–emission fluorescence matrix of antioxidant was done on a Hitachi (Japan) F-4500 equipped with a xenon lamp. The excitation and emission slit widths were 5 nm. EEM was registered in the following ranges: λ_{ex} = 210–320 nm each 1 nm and λ_{em} = 300–470 nm each 2 nm with a scanning rate of 12,000 nm/min. All samples were carried out using 1.00 cm quartz cells. The spectra were saved and translated into a suitable format. And then the three-way data were set up. Finally, SWANRF algorithm was applied to the decomposition of the three-way array formed by stacking the EEM for calibration samples and prediction samples.

3.4. High-performance liquid chromatography (HPLC) analysis

HPLC was performed using a Shimadzu (Japan) LC-20AT equipped with a degasser, a pump, a manual injector provided with a 20 μl loop, a column oven and a diode array detector (DAD). The absorbance was measured at 280 nm. Chromatographic separation of BHA, PG and background was achieved at 25 °C using a Hypersil-ODS C18 column (5 μm average particle size, 150 mm × 4.6 mm i.d.). The mobile phase consisted of methanol and acetonitrile (1:1 v/v, solvent A), and 0.1% formic acid in water (solvent B). The column was equilibrated in 20% A and the gradient was 20–100% A over 15 min, hold at 100% A for 0.5 min, 100–20% A over 0.5 min, hold at 20% A for 1 min. A flow rate of 1 μl/min was used; injection volume was 20 μl. Quantitative determination was based on peek area as the analytical parameter. According to manufacturer instructions, data were processed.

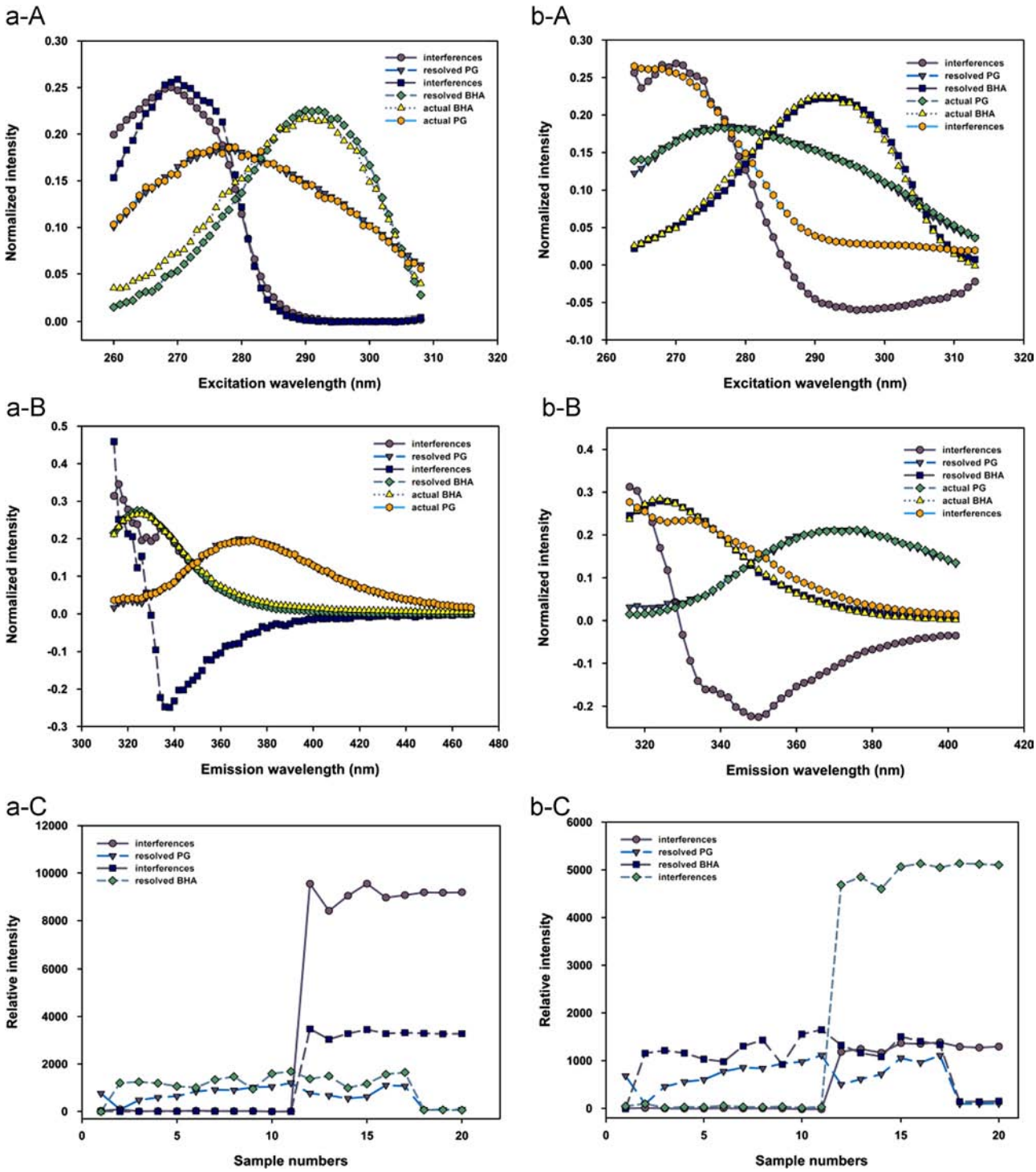

Fig. 2. The profiles of normalized excitation (a-A, b-A), normalized emission (a-B, b-B) and relative concentration (a-C, b-C), obtained from the SWANRF method (left for latex and right for emulsion), and the actual spectral profiles of butylated hydroxyanisole (BHA) and propyl gallate (PG).

4. Results and discussion

4.1. EEM with SWANRF

4.1.1. Excitation–emission fluorescence matrix (EEM)

Fig. 1 reveals the three-dimensional plots corresponding to the excitation–emission fluorescence matrix (EEM) for the pure BHA, the pure PG, and two cosmetics samples in wide spectral excitation and emission ranges, showing the presence of both Rayleigh and Raman scatterings. To avoid the presence of signals that are uncorrelated with the target concentrations of the analytes of interest and do not conform to the trilinear model, EEM, as a general rule, should be truncated. That is why the spectral excitation and emission ranges should be changed. The spectral surfaces of latex samples were recorded at excitation wavelengths varying from 260 to 308 nm, and emission wavelengths varying from 314 to 468 nm. The spectral surfaces of emulsion samples were recorded at excitation wavelengths varying from 264 to

313 nm, and emission wavelengths varying from 316 to 402 nm. And then the calibration samples and the prediction samples were stacked into two cubes (one for latex, another for emulsion).

4.1.2. Cosmetics samples

With the purpose of building a second-order calibration model, EEM was recorded for the calibration samples which only contained BHA and/or PG. The concentration ranges and regression data related to the calibration line for each analyte is presented in Table 5. As observed, the linearity of the analytical response within the studied concentration range is excellent, with correlation coefficients higher than 0.99. Twelve spiked cosmetics samples, consisting of BHA, PG (Table 1) and cosmetics are the prediction samples. The number of components when SWANRF was applied was selected by the so-called core consistency analysis [35]. It consists in studying the structural model based on the data and the estimated parameters of gradually augmented models. The estimated number of components was four, which can be justified taking into account the presence of four different signals (corresponding to BHA, PG and two interferences) in the selected region. After subtracting the corresponding solvent blank, the new three-way data was analyzed by SWANRF algorithm with $N=4$.

Fig. 2 displays the actual spectral profiles, the resolved spectral profiles and the relative concentration profiles corresponding to the application of SWANRF algorithm. It is clear in this figure that overlapping occurs among the excitation and the emission spectra and the unknown interferences, which hinders the direct spectrofluorimetric determination of BHA and PG. And the response intensity of these interferences are much higher than the interesting analytes. Therefore, with the purpose of overcoming the overlapping problems, a chemometric analysis was intended.

Finally, the satisfactory prediction results were obtained by the SWANRF method. The resolved spectra coincide well with the fluorescence spectra actually measured in BHA and PG individually, which are shown in Fig. 2(a-A, a-B, b-A and b-B). The results of recovery of BHA and PG in each type of cosmetic are shown in Table 1. The average recoveries of BHA and PG are $101.4 \pm 1.8\%$ and $101.8 \pm 2.3\%$ in latex samples, $97.6 \pm 1.2\%$ and $100.3 \pm 1.5\%$ in emulsion samples, respectively. The concentration ranges in which studied components could be determined are as follows: BHA, 0.00437–0.0151% and PG, 0.0107–0.0583% in the cosmetics samples. A performance characteristic of the SWANRF calibration method also furnishes interesting figures of merit. The analytical figures of merit, such as sensitivity (SEN) [36], limit of detection (LOD) [33] and limit of quantification (LOQ) [34], are shown in Table 2. The present study demonstrated that our method enables one to detect BHA and PG at sufficiently low limits.

4.2. HPLC

The high-performance liquid chromatography (HPLC) method is based on the AOAC official method 983.15(1994). Because of the differences of the chromatographic column and the cosmetics, the condition of the reference method should be improved, such as mobile phase, flow rate and column temperature. The separation behaviors using the following mobile phases: aqueous methanol, aqueous methanol containing 10% water, aqueous methanol–acetonitrile (1:1 v/v) and aqueous water containing 1% formic acid were investigated, respectively. The separation was also investigated under different gradient elution conditions. Using gradient elution conditions described in Section 3.4, BHA, PG and backgrounds can be separated properly with symmetrical peak shapes, which is shown in Fig. 3.

For the analytical signals, either the height or the area of the peaks could be used. The calibration graphs are linear for both analytes in the range 8.31–33.4 μg/ml using area as the parameter. The linear regression equations and correlation coefficients are shown in Table 5. And then, the results obtained for the predicted BHA and PG concentrations in two cosmetics samples are shown in Table 3. BHA and PG can be quantified at concentration ranges of 0.0170–0.0513% and 0.0171–0.0518% in the cosmetics specimens, respectively.

4.3. Comparison of two methods

The two methods were compared with regard to dosage of cosmetics and organic reagents, runtime, cost and limit of detection (LOD). A summary of the comparison is given in Table 4. The HPLC method requires all solutions filtered through 0.45 μm nylon filters, which is not needed in our method. The dosage of cosmetics needed for HPLC analysis is 400–440 mg, while 6.74–7.38 mg is required for EEM–SWANRF. The reason is that the sensitivity of HPLC is inferior to the fluorescence. The EEM–SWANRF method is approximately 7 times faster and 10 times cheaper than the HPLC method. In addition, one of the main advantages of our method is that it uses very small amounts of organic reagents. The quantification of PG and BHA was accomplished using green-chemistry principles. On the contrary, the HPLC method may take a long time and/or complex mobile phase to isolate each of the analytes to provide accurate results, which involves timeconsuming and consuming large amount of organic solvents. There was every sign to show that EEM–SWANRF is more satisfactory for simultaneous determination of BHA and PG in the cosmetics samples.

In addition, the HPLC cannot be guaranteed the versatility when the analytes are in different systems and the chromatographic conditions may need to re-establish. Relative to the

Table 1
Recovery study of BHA and PG in cosmetics samples using SWANRF.

Sample	Latex				Sample	Emulsion			
	BHA (μg/ml)		PG (μg/ml)			BHA (μg/ml)		PG (μg/ml)	
	Taken	Found[a]	Taken	Found[a]		Taken	Found[a]	Taken	Found[a]
PF1	0.0912	0.0923(101.2)	0.13972	0.1422(101.8)	PF7	0.0911	0.0913(100.2)	0.0998	0.1001(100.3)
PF2	0.0995	0.1009(101.4)	0.11976	0.1246(104.1)	PF8	0.0829	0.0793(95.7)	0.11976	0.1220(101.8)
PF3	0.0622	0.0646(103.9)	0.0998	0.1022(102.4)	PF9	0.0746	0.0733(98.3)	0.13972	0.1429(102.2)
PF4	0.0746	0.0769(103.1)	0.10978	0.1160(105.7)	PF10	0.1077	0.1046(97.1)	0.20958	0.2111(100.7)
PF5	0.1077	0.1062(98.6)	0.20958	0.2047(97.7)	PF11	0.0995	0.0975(98.0)	0.1996	0.1913(95.9)
PF6	0.1119	0.1120(100.1)	0.1996	0.1978(99.1)	PF12	0.0953	0.0919(96.5)	0.21956	0.2221(101.2)
Average recovery (%)	101.4 ± 1.8		101.8 ± 2.3			97.6 ± 1.2		100.3 ± 1.5	

[a] Recovery in parentheses.

Table 2
Analytical figures of merit of the SWANRF method for cosmetics samples.

Figure of merit	Latex		Emulsion	
	BHA	PG	BHA	PG
SEN/ml ng^{-1}	38.1	0.9	208.6	1.8
LOD/ng ml^{-1}	1.3	2.9	1.2	2.2
LOQ/ng ml^{-1}	3.8	8.8	3.7	6.7

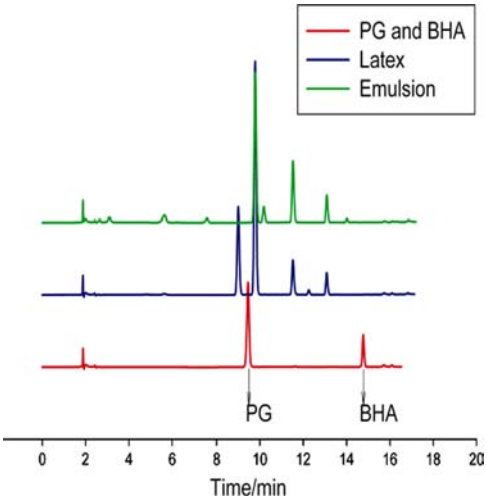

Fig. 3. Liquid chromatograms of two antioxidants mixture (16.6 μg/ml of butylated hydroxyanisole (BHA) and 18.8 μg/ml of propyl gallate (PG)) and two cosmetics samples (0.42 g of latex and 0.41 g of emulsion). Condition: flow rate, 1.0 ml/min; sample volume, 20 μl; mobile phase, methanol–acetonitrile (1:1 v/v) and water (1% formic acid), gradient elution; λ=280 nm.

Table 3
Recovery study of BHA and PG contents in cosmetics samples using HPLC.

		BHA (μg/ml)		PG (μg/ml)	
		Taken	Found[a]	Taken	Found[a]
Latex	PC1	10.4	11.1 (106.7)	8.36	8.41 (100.6)
	PC2	16.6	17.6 (106.0)	14.6	15.5 (106.2)
	PC3	22.8	21.7 (95.2)	20.9	20.3 (97.1)
Emulsion	PC4	8.31	8.80 (105.9)	10.4	10.3 (99.0)
	PC5	14.5	15.1 (104.1)	16.7	16.8 (100.6)
	PC6	20.8	21.0 (101.0)	23.0	22.4 (97.4)

[a] Recovery in parentheses.

Table 4
Method comparison.

Method	EEM-SWANRF	HPLC
Dosage of cosmetics	6.74–7.38 mg	400–440 mg
Runtime	3.5 min	23 min
Cost per analysis	$0.06–0.16	$0.72–1.67
LOD	1.2–2.9 ng/ml	150.0–200.0 ng/ml
Dosage of organic reagents	Small	Large

EEM–SWANRF, it can be applied to different systems and the conditions could be the same. This useful property benefit from second-order advantage. However, matrix effects, for example partial fluorescence quenching of the analyte of interest, often occur [18]. In those cases, the second-order standard addition method [37] or a four-way model [38] as a mean of overcoming matrix or background effects is recommended to ensure accurate results.

Table 5
Concentration ranges and regression data used for the analytes of interest.

Method	Analyte	c (μg ml^{-1})	Regression equation[a]	R
SWANRF	PG	0.09–0.22	$Y=4.84\times10^{3}X+18.42$	0.9905
	BHA	0.06–0.12	$Y=1.33\times10^{4}X+142.00$	0.9940
HPLC	PG	8.36–33.40	$Y=4.56\times10^{4}X+1.71\times10^{4}$	0.9990
	BHA	8.31–29.10	$Y=1.58\times10^{4}X-1.17\times10^{4}$	0.9980

[a] X is concentration and Y is response.

5. Conclusions

The novel method is alternative to simultaneous determination of BHA and PG in cosmetics samples, due to its higher speed, efficiency, reproducibility, much smaller organic reagents and sample volume and more ease of pretreating the complex matrix. It is assisted by chemomeric second-order calibration employing the self-weighted alternating normalized residue fitting (SWANRF) algorithm. The named 'second-order advantage' is sufficiently utilized, which would help the researchers obtain qualitative and quantitative information of interested species in the presence of uncalibrated interferences and the background. Compared to the HPLC method (the AOAC official method 983.15(1994)), the EEM–SWANRF is a more sensitive, simpler, faster, cleaner and more powerful method. Even though in this report only two antioxidants have been quantified, it seems observable that the quantification of a higher number of antioxidants could be performed.

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