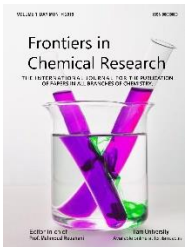

Fron.Chem. Res, 2020, Vol: 2, Issue: 1, pages: 1-9.

Frontiers in Chemical Research

Research article

Ilam University

Comparison between univariate and multivariate calibration methods for simultaneous spectrophotometric determination of catechol and hydroquinone in their binary mixture

Ghadamali Bagherian*, Fatame Salehi Mobarake, Mansour Arab Chamjangali, Motahare Ashrafi, Haniye Borzooei

College of Chemistry, Shahrood University of Technology, Shahrood, P.O. Box 36155-316, Iran.

Received: 07 November 2019
Accepted: 22 February 2020
Published online: 20 April 20

Abstract Two novel univariate calibration methods, namely the extended ratio subtraction method (EXRSM) and the simultaneous ratio subtraction method (SRSM) were employed for the simultaneous determination of catechol (CT) and hydroquinone (HQ) in synthetic binary mixtures. The precision, accuracy, and specificity of these methods were statistically compared to those obtained from the derivative method (as a univariate calibration method), and the principal component regression (PCR) and the partial least squares (PLS) methods (as two multivariate calibration methods). Comparison of the results showed that there was no significant difference between the proposed methods. The main advantages of the proposed methods are that, unlike the other analytical methods, it is not necessary to use expensive apparatus and chemicals, and that they can be easily performed using a simple spectrophotometer that is available in all quality control labs. The developed methods were successfully applied for the simultaneous determination of CT and HQ with different ratios in tap water as the real sample.

Keywords: Catechol; Hydroquinone; Chemometric; Extended ratio subtraction method; Simultaneous ratio subtraction method.

1. Introduction

Catechol (1, 2-dihydroxybenzene, CT) and hydroquinone (1, 4-dihydroxybenzene, HQ) (Fig. 1) which are isomers of dihydroxybenzene [1] usually coexist in biological and environmental samples [2]. They are produced during biological degradation processes, and are commonly found in a wide variety of industries such as the cosmetic, plastic, dye, and pharmaceutical ones [3- 5]. These environmental pollutants are toxic to the humans, and are difficult to degrade in ecological environments [3]. Therefore, the simultaneous determination of their concentration is an interesting and demanding subject in environmental analysis [2]. At the present time, various methods; including, the spectrophotometry [6, 7], chemiluminescence [8, 9], chromatography [10-12], fluorescence spectroscopy [13], capillary electro-chromatography [14], pH-based flow injection analysis [15], and electrochemical [1, 16-19] techniques are used for the determination of these phenolic pollutants. Among these analytical methods, the spectrophotometric methods are cheaper, faster, and simpler. However, overlapping absorption peaks of isomers limit the use of the traditional spectrophotometric techniques [20]. Recently, the researchers have shown that the novel spectrophotometric methods, such as the extended ratio subtraction method (EXRSM) and the simultaneous ratio subtraction method (SRSM), can resolve this problem. These methods are able to recover the zero-order absorption spectra of both compounds from their binary mixtures through simple mathematical calculations [21].

The aim of the present work is to determine the concentrations of HQ and CT in binary mixtures by the cited methods, and to conduct a comparative study between the univariate and multivariate methods in resolving the spectrally overlapped bands. The studied univariate methods are the EXRSM, SRSM, and derivative techniques, while the multivariate calibration methods are the principal component regression (PCR) and partial least squares (PLS) methods.

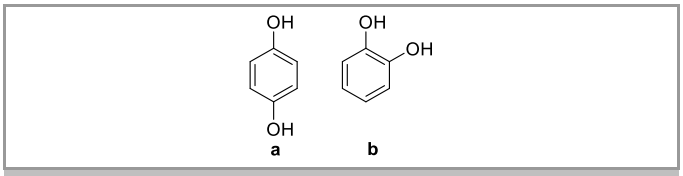

Figure 1. Chemical Structures of (a) HQ and (b) CT.

The novelty of the ongoing work is that the employed methods are simpler, faster, cheaper, and less time-consuming than the other methods cited in the literature.

2. Theory

Theories of the EXRSM [22], SRSM [23], derivative [24, 25], PCR [26] and PLS [26- 28] methods have been published.

3. Experimental

3.1. Materials, instruments, and software

CT and HQ (Fig. 1) were supplied from Sigma-Aldrich. Standard stock solutions of CT or HQ were prepared by dissolving 0.0500 g of CT or HQ in 100 mL of water. The working standard solutions for each analyte were prepared by diluting appropriate volumes of these stock solutions. Doubly distilled water was used throughout the work.

A Rayleigh UV-2601 spectrophotometer was employed to record the absorption spectra of the reference and test solutions in 1.0 cm quartz cells over the range of 210-310 nm at 0.5 nm intervals. To measure the solution pH, a pH-meter (Model 744) equipped with a combined electrode was used. The PCR and PLS programs were written in the Matlab software. Moreover, smoothing of the derivative spectra was made using a Savitzky-Golly filter in the Matlab software (Math Work; Inc.; Natick; MA; USA).

3.2. Procedure for construction of individual calibration

In order to prepare each standard sample solution, an aliquot of a solution containing 5.0-500.0 µg of HQ or 5.0-800.0 µg of CT, and 2.0 mL of a buffer solution (with pH 7.0) was added to a 10-mL

*Corresponding author: Ghadamali Bagherian, Email: Gh_Bagherian@shahroodut.ac.ir Tel: +98 23 32395441

volumetric flask, and the resulting solutions were diluted to the mark with doubly distilled water. A portion of each solution was transferred into a quartz cell. The spectra of the prepared standard solutions against a reagent blank were scanned from 210 to 310 nm and, then, stored in a computer. The individual calibration curves were constructed by depicting the absorbance of the zero-order spectra vs. their corresponding concentrations at λmax = 275 nm for CT and λmax = 286.5 nm for HQ. The linear regression equations A = 0.0195 CCT + 0.0131 (R2 = 0.9986, n = 13) and A = 0.0233 CHQ + 0.0013 (R2 = 0.9999, n = 12) were obtained for CT and HQ, respectively. In these equations, A is the absorbance of each sample solution against a reagent blank, and CHQ and CCT are the concentrations of HQ and CT, respectively, in µg/mL.

3.3. Procedure for simultaneous analysis of CT and HQ in binary solutions

The scanning profile of the two isomers (Fig. 2) show that due to the spectral overlapping, an accurate determination of CT and HQ in their binary mixture was not possible by a direct UV–visible absorbance measurement. To overcome this problem, the different univariate and multi-variate calibration methods (such as EXRSM, SRSM, derivative, PLS, and PCR) were examined.

3.3.1. Univariate methods

3.3.1.1. Extended ratio subtraction method (EXRSM)

Aliquot equivalents of 40-150 µg of CT and 60 µg of HQ were transferred from their working standard solutions into 10-mL volumetric flasks. Then, 2.0 mL of a phosphate buffer

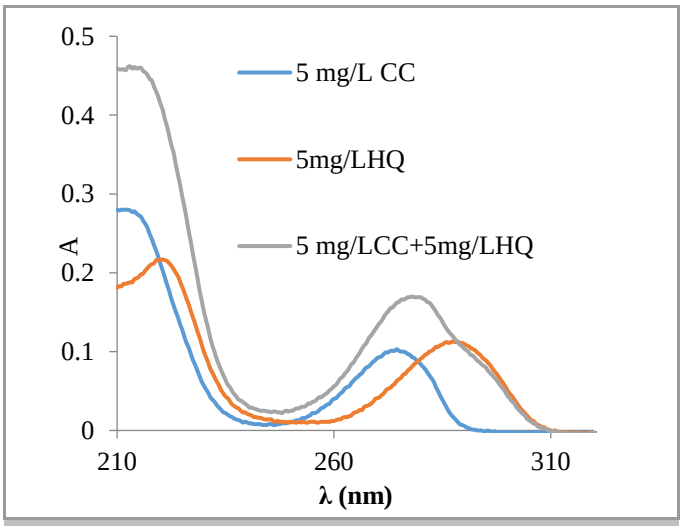

Figure 2. Absorption spectra for CT and HQ in single and binary solutions.

solution (pH = 7.0) was added, and the solutions were diluted to the mark with water. The spectra for the resulting standard solutions, recorded from 210–310 nm, were divided by a carefully selected concentration of HQ (20 µg/mL) as a divisor (CHQ) (Fig. 3). As it can be seen in this figure, the relative spectra obtained in the wavelengths greater than 290 nm (the region in which the spectrum for HQ is more extended than that for CT) had a constant value for the above mixtures. This constant value representing the CHQ/CHQ ratio (ratio of the concentration of HQ in binary solutions to the divisor solution), was subtracted from the relative spectra (Fig. 4) and, then, multiplied by the spectrum of the divisor (Fig. 5). In this sense, the pure spectra for 4, 7, 9, 12, and 15 µg/mL of CT were obtained. Using the pure obtained spectra, the absorbance was measured at the maximum wavelength (275 nm) for CT and, then, placed in the calibration curve obtained from pure standard solutions of CT and, finally, its concentration in each mixture was obtained.

To obtain the HQ concentration in the prepared mixtures, the pure zero-order spectra obtained for CT (Fig. 5) were divided by a carefully chosen divisor of CT (e.g. 15 µg/mL). The resulting ratio spectra in the range of 265-280 nm had a constant value, which is parallel to the wavelength axis for each solution (Fig. 6).

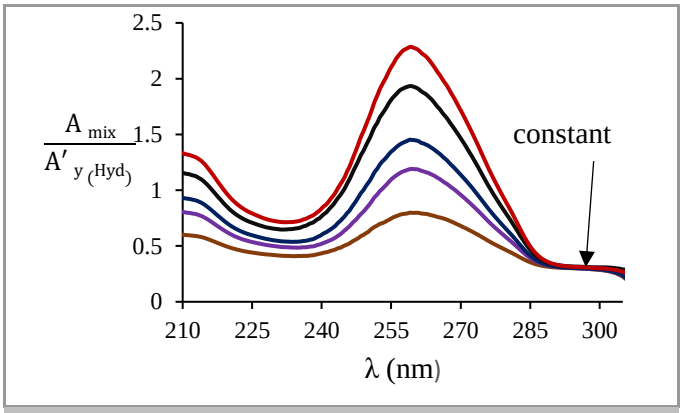

Figure 3. Ratio spectra for binary mixtures of CT (4, 7, 9, 12, and 15 µg/mL) and HQ (6 µg/mL) using 20 µg/mL of HQ as a divisor..

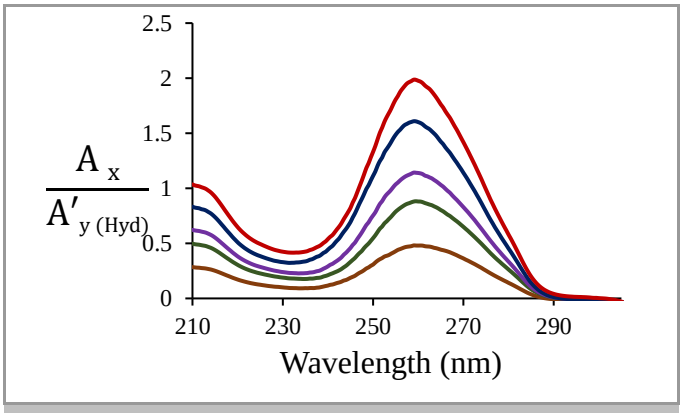

Figure 4. Ratio spectra for binary mixtures of CT (4, 7, 9, 12, and 15 µg/mL) and HQ (6 µg/mL) using 20 µg/mL of HQ as a divisor after subtraction of the constant.

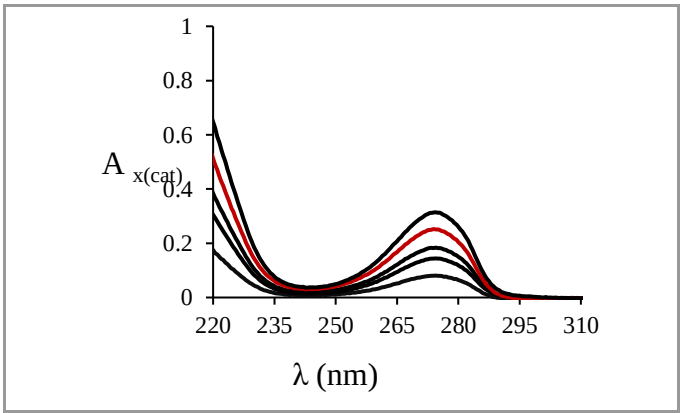

Figure 5. Zero-order absorption spectra for CT (4, 7, 9, 12, and 15 µg/mL) after subtraction of the constant and multiplication by the spectrum for 20 µg/mL of HQ as a divisor.

Also, the zero-order absorption spectra for the binary mixtures (4, 7, 9, 12, and 15 µg/mL of CT and 6 µg/mL of HQ) were divided with a specific concentration of CT solution (e.g. 15 µg/mL) (Fig. 7).

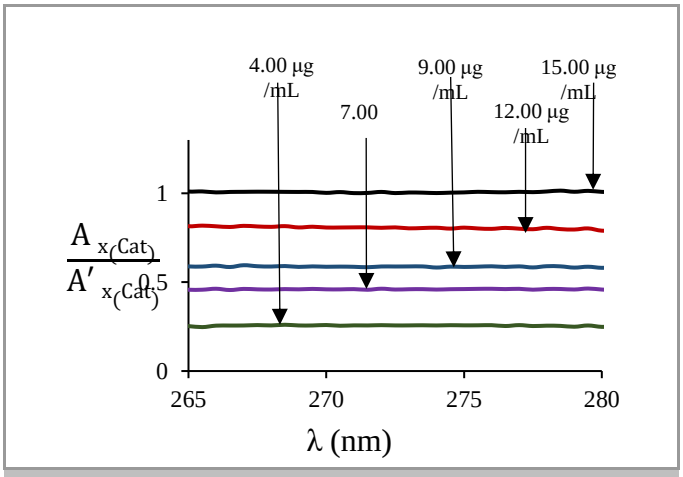

Figure 6. Ratio spectra for CT (4, 7, 9, 12, and 15 µg/mL) using the spectrum of 15 µg/mL of CT as divisor.

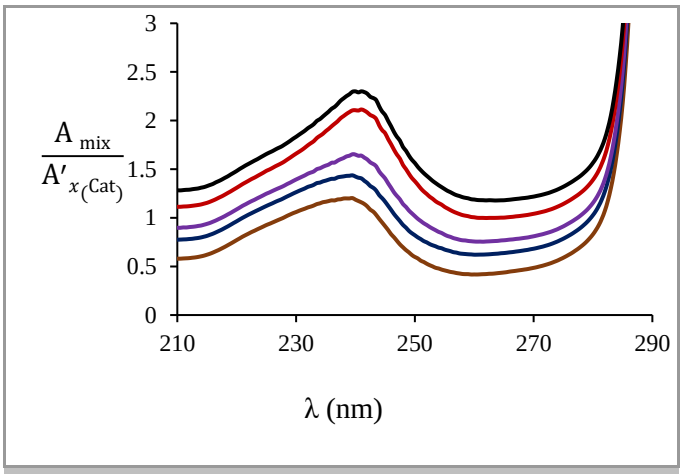

Figure 7. Ratio spectra for binary mixtures of CT (4, 7, 9, 12, and 15 µg/mL of CT) and 6 µg/mL of HQ using 15 µg/mL of CT as a divisor.

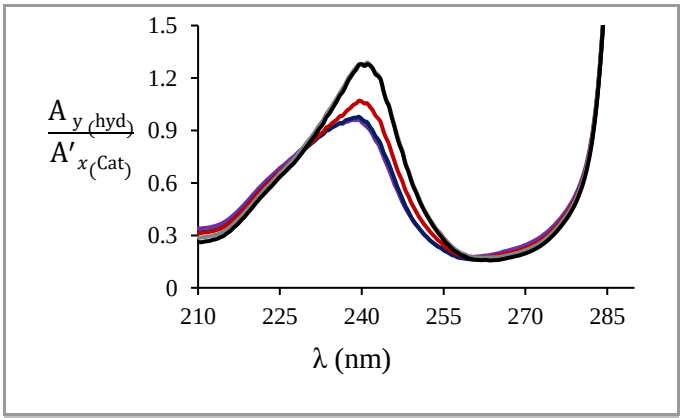

Figure 8. Ratio spectra for binary mixtures of CT (4, 7, 9, 12, and 15 µg/mL of CT) and 6 µg/mL of HQ using 15 µg/mL of CT as a divisor after subtraction of constants.

Afterwards, the previously obtained constants (Fig. 6) were subtracted from the relative spectrum of its corresponding mixture (Fig. 7). By multiplication of the relative spectra obtained from the previous step (Fig. 8) by the spectrum of 15 µg/mL of standard CT, the pure spectrum of HQ was obtained (Fig. 9). Therefore, by measuring the absorbance at the maximum wavelength of the pure zero-order spectra for HQ and the corresponding calibration curve, its concentration in each mixture was estimated.

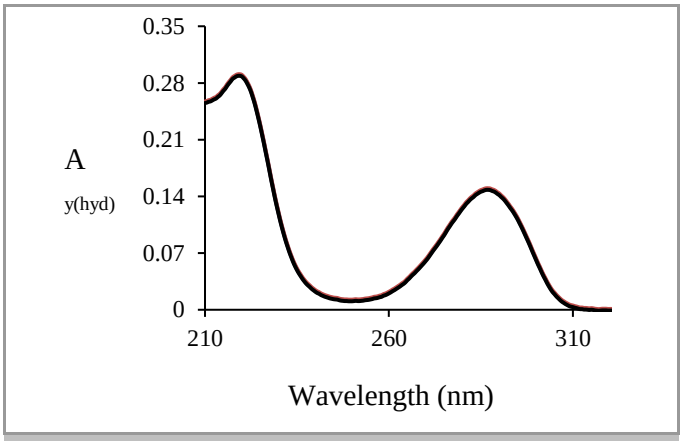

Figure 9. Zero-order absorption spectrum for HQ (6 µg/mL) after multiplication by the spectrum of 15 µg/mL of CT.

3.3.1.2. Simultaneous Ratio Subtraction Method (SRSM)

Aliquot equivalents of 40-150 µg of CT and 60 µg of HQ were transferred from their working standard solutions into 10-mL volumetric flasks. Subsequently, 2.0 mL of a phosphate buffer solution (pH = 7.0) was added and the solutions were diluted to the mark with water in order to obtain concentrations from 4 to 15 µg/mL of CT. The spectra for the resulting standard solutions were recorded using a spectrophotometer from 210 to 310 nm with intervals of 0.5 nm. The spectra for the prepared mixtures were divided by the spectrum for 20 µg/mL of HQ (Fig. 3). Then, the constant in the plateau region (wavelength range of 290-300 nm) was subtracted from the obtained ratio spectra (Fig. 4). After using amplitudes of the ratio spectra at 275 nm for each mixture and the regression equation representing correlation between the amplitudes of ratio spectra and the corresponding concentration of CT, the concentration in each mixture was calculated. In order to obtain the HQ concentration, the pure standard solutions of HQ were divided by a specific concentration of HQ. By measuring the constant value for all standard solutions, the calibration plot representing the correlation between the constant values and HQ concentrations were depicted. Then, using the obtained calibration equation and the acquired constant values for each mixture (Fig. 3), the HQ concentration was computed.

3.3.1.3. Derivative method

Another technique used to resolve the spectral overlapping was the derivative method. In this method, by measuring the derivative value at the wavelength where the impact of the other component is negligible, the best calibration curve is available. In the present work, the first-order derivative (1D) method was employed to simultaneously analyze CT and HQ in binary mixtures since, with respect to the higher-order derivative methods, the first-derivative spectra have a high signal-to-noise ratio (S/N).

According to the first-order derivative spectra obtained for CT and HQ for the single and binary mixtures (Fig. 10), the cited isomers could be determined at 287 nm and 299 nm (regions where the other isomer has no contribution), respectively. Therefore, the calibration equation for CT and HQ was computed using its first-order signal at 287 nm and 299 nm vs. their different concentrations. The linear

regression equations A = - 0.001322CCT - 0.00052 (R2 = 0.9977) and A = - 0.001750CHQ - 0.000136 (R2 = 0.9998) were obtained for CT and HQ, respectively.

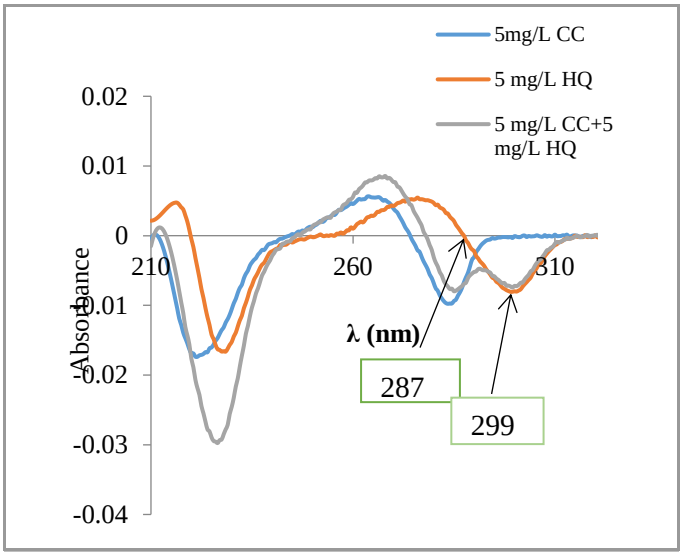

Figure 10. First-order absorption spectra for CT and HQ in single and binary solutions.

3.3.2. Multivariate method

3.3.2.1 PCR and PLS methods

For implementation of the PCR and PLS methods, a calibration set of 30 mixtures whose concentrations lied in their linear dynamic range (Table 1) was designed. This subset was used to optimize the number of latent variables [28, 29].

4. Results and discussion

The main objective of the present work was to create simple, sensitive and accurate analytical methods for the simultaneous determination of CT and HQ in their binary mixture solution with high accuracy. With respect to other analytical techniques, the important features of the spectrophotometric methods are the availability of the instrumentation, the simplicity of procedures, speed, precision, and accuracy of the technique [30]. The spectrophotometric methods developed in this work require a minimum sample preparation and use solvents that are not dangerous to the environment.

Novel methods: EXRSM and SRSM are two novel spectrophotometric techniques established for determination of CT and HQ in binary mixtures without preliminary separation. For employing the EXRSM and SRSM methods, the only requirement is that, in the studied mixture, the spectrum of a substance be more extended than the other one. As shown in Fig. 2, the spectrum for HQ is more extended than the spectrum for CT, so the cited methods could be used for their simultaneous analysis. These methods are very simple, rapid, and accurate, and the two isomers can be determined in mixture with the help of a pure zero-order spectrum, which was obtained from the mixed spectrum using simple mathematical computations.

In order to achieve a better selectivity and minimum error in the simultaneous determination of the isomers, the influence of the concentration used as the divisor must be investigated. An appropriate divisor is the one that gives the best regression equation [31], and thus a minimum error in the prediction of analyte concentration in the mixture systems. The obtained results (Tables 2 and 3) show that there is no significant difference between the prediction errors when different concentrations of CT or HQ are selected as the divisor.

Table 1. Combination of the different mixtures of CT and HQ used in the calibration set.

Sample	CT (µg/mL)	HQ (µg/mL)
1	1.00	1.00
2	1.00	3.00
3	1.00	6.00
4	1.00	9.00
5	1.00	12.00
6	4.00	1.00
7	4.00	3.00
8	4.00	6.00
9	4.00	9.00
10	4.00	12.00
11	7.00	1.00
12	7.00	3.00
13	7.00	6.00
14	7.00	9.00
15	7.00	12.00
16	9.00	1.00
17	9.00	3.00
18	9.00	6.00
19	9.00	9.00
20	9.00	12.00
21	12.00	1.00
22	12.00	3.00
23	12.00	6.00
24	12.00	9.00
25	12.00	12.00
26	15.00	1.00
27	15.00	3.00
28	15.00	6.00
29	15.00	9.00
30	15.00	12.00

Table 2. Results of optimization of HQ concentration as a divisor in prediction of CT concentration in binary mixtures.

CHQ (µg/mL)	MSE in prediction of CT concentration
5.00	0.004
10.00	0.004
15.00	0.004
20.00	0.004
25.00	0.004

Table 3. Results of optimization of CT concentration as a divisor in prediction of HQ concentration in binary mixtures.

CHQ (µg/mL)	MSE in prediction of HQ concentration
5.00	0.0086
10.00	0.0086
15.00	0.0086
20.00	0.0086
25.00	0.0086

Derivative method: The derivative spectrophotometric method is useful for improving the resolution of mixtures and minimization or elimination of background absorption without a previous chemical separation. Taking into account this important feature, the derivative technique was employed for the simultaneous determination of CT and HQ. By measuring the peak amplitude at 287 nm and 299 nm (where there is no contribution from other compounds) and the corresponding calibration equation, the CT and HQ concentrations can be determined.

In this method, the influence of Δλ variables on prediction of analyte concentration was studied, in which a minimum error was acquired at Δλ = 0.5 nm. Moreover, the higher-order derivative methods were also studied. However, it was observed that with increase in the derivative order, the noise level also increased.

Multivariate methods: As shown in Table 1, for the calibration and external test sets, different mixtures of CT (1-15 µg mL^{-1}) and HQ (1-12 µg mL^{-1}) were prepared in the laboratory. The spectral data was collected in the range of 210-310 nm at intervals of 0.5 nm. Thus, the generated spectral data matrix shows 30 rows illustrating different samples and 201 columns showing wavelength (30 × 201). Choosing the optimal number of factors for the PCR and PLS methods was a very important step before building the models due to the fact that if the number of the preserved factors was more than needed, more noise would be added to the data. In contrast, if the retained factors were too small, the significant data essential for the calibration of data might be discarded. Different methods can be used to determine the optimal number of factors [31]. In this work, to select the optimum number of factors, the leave-one-out cross-validation technique [32] was used, and minimization of root mean square error (RMSE) of the calibration data (Eq. (1)) was selected as a criterion in the optimization process.

$$RMSE = \sqrt{\frac{\sum(\hat{C}_i - C_i)^2}{N}} \qquad (1)$$

where C_i is the theoretical concentration of the analyte i, $\hat{C}_i$ is the estimated (predicted) concentration of the analyte i, and N is the number of calibration samples. In this regard, RMSE was calculated for the first latent variable, which built the PLS model in the calibration step. Then, the second latent variable was added, and RMSE was computed again. For 1-15 latent variables, the computations were reiterated. The number of latent variables giving the minimum RMSE was chosen for modeling. According to Fig. 11, in the PCR method, a number of latent variables of 5 and 3 were selected as the optimum ones for CT and HQ, while in the PLS method, the number of latent variables of 3 was selected as the optimum one for both isomers.

4.1. Validation of proposed methods in determination of CT and HQ in laboratory prepared mixtures

4.1.1. Specificity

Specificity of the proposed methods was investigated by analyzing CT and HQ in the laboratory prepared mixtures with different concentrations, and the obtained results were tabulated in Tables 3 and 4, respectively. The results demonstrate that the specificity of the novel methods is comparable to that of the multivariate methods.

4.1.2. Accuracy and precision of proposed methods

In order to evaluate the accuracy of the proposed methods, solutions with different concentrations of CT (1, 3, 15, and 2 µg mL^{-1}) and HQ (3, 9, 5, and 2 µg mL^{-1}) were determined using the proposed methods as depicted in Tables 5 and 6. The predicted concentrations and the relevant standard deviations show that the proposed methods have a suitable accuracy and precision.

4.1.3. Limit of detection (LOD)

The detection limits for the univariate methods were determined using the following equation:

LOD = 3 (SD (blank))/m (2)

where SD and m are the standard deviation of the blank signal and the slope of the regression curve, respectively. Therefore, based on this equation for determination of the detection limit of the EXRSM, SRSM, and derivative methods, 10 repeated measurements (in the wavelength range of 210-310 nm) were performed for the blank solution. Then, three times the standard deviation of the blank signal to the slope of the calibration curve was recognized as the detection limit. For the PCR and PLS methods, the absorbance of ten blank solutions was recorded from 210-310 nm. Using the optimized models constructed by the PCR or PLS models; the concentration was predicted. Afterwards, three times the standard deviation of the predicted concentration for each analyte was considered as the detection limit [32]. The results obtained for the cited methods were tabulated in Tables 4 and 5, respectively.

4.1.4. Interference Study

In order to evaluate the ability of the methods to simultaneously determine CT and HQ in the real samples, the effects of the different interfering species were studied. This investigation was done as what follows: absorbance of 2.00 µg/mL of the CT or HQ solution was measured for six times at the maximum wavelengths of 275 and 286.5 nm, respectively. Then, the mean and standard deviations of absorbance were calculated, and the confidence interval ($\bar{A} \pm 3S_A$) was obtained for each compound. If the absorbance of the solution contained HQ or CT and a certain concentration of foreign species was outside the range of its confidence interval, it was considered as the interference. The obtained results are shown in Table 8. Resorcinol is another isomer of dihydroxyphenol. Therefore, it has an absorbance in the wavelength range of 210–310 nm. Due to the presence of benzene ring in the phenol structure, an absorbance in the range of 210-310 nm is observed. The maximum absorption wavelengths of nitrite are 280 and 360 nm. Therefore, the interference caused by the resorcinol, phenol, and nitrite species is of the blank interference type. Most foreign species did not interfere with the determination even if they were present in amounts 200-fold greater than HQ or CT. The obtained results demonstrate that the EXRSM and SRSM methods have a good selectivity.

4.1.5. Application of proposed methods in analysis of real samples

The proposed methods were successfully applied for the simultaneous determination of CT and HQ in tap water as the real sample using the standard addition technique.The concentrations were calculated using the corresponding regression equations (Tables 9 and 10). The obtained results which were satisfactory imply that the proposed methods are suitable for the quantification of these isomers in real samples.

Table 4. Determination of CT and HQ in their laboratory binary mixtures by univariate spectrophotometric methods.

Concentration (μg/mL)		EXRSM method		SRSM method		1D method	
CT	**HQ**	**Recovery (CT)**	**Recovery (HQ)**	**Recovery (CT)**	**Recovery (HQ)**	**Recovery (CT)**	**Recovery (HQ)**
2.00	**3.00**	103.50	101.33	105.00	103.00	83.74	101.22
3.00	**6.00**	100.00	99.17	103.33	100.88	101.47	100.54
5.00	**4.00**	101.6	102.50	102.00	102.50	96.77	102.07
8.00	**5.00**	100.13	101.80	101.12	102.00	100.07	102.70
8.00	**8.00**	99.13	99.125	101.25	100.75	102.72	99.79
10.00	**4.00**	99.30	103.25	100.90	104.00	97.19	101.66
10.00	**6.00**	99.60	100.33	100.3	101.33	98.93	102.61
10.00	**9.00**	99.30	99.44	100.9	100.00	100.49	98.87
14.00	**2.00**	100.29	102.00	101.00	102.50	100.50	110.88
15.00	**4.00**	99.73	101.00	99.80	99.50	99.24	107.77
Mean		100.25	100.99	101.56	101.67	98.05	102.81
RMSE		0.056	0.070	0.093	0.083	0.17	0.14
RSD(%)		0.69	1.46	1.15	1.74	2.11	3.00
R2*		0.9999	0.9995	0.9999	0.9995	0.9986	0.9982
Linear range		1-15	1-12	1-15	1-12	1-15	1-12
LOD		0.169	0.0745	0.132	0.132	0.21	0.19

*Data for the straight line plotted between the predicted concentrations against the real concentrations.

Table 5. Determination of CT and HQ in their laboratory binary mixtures by multivariate spectrophotometric methods.

Concentration (μg/mL)		PCR method		PLS method	
CT	**HQ**	**Recovery (CT)**	**Recovery (HQ)**	**Recovery (CT)**	**Recovery (HQ)**
2.00	3.00	99.31	103.97	102.99	104.01
3.00	6.00	100.24	100.98	105.16	100.97
5.00	4.00	100.62	102.55	101.78	102.53
8.00	5.00	99.62	100.83	101.38	100.78
8.00	8.00	100.15	99.09	102.24	99.02
10.00	4.00	99.38	101.12	100.59	101.02
10.00	6.00	98.36	99.54	99.92	99.50
10.00	9.00	99.48	98.45	101.50	98.37
14.00	2.00	101.27	102.47	100.91	102.54

15.00	4.00	98.15	102.71	99.29	102.71
No. of factors		5	3	3	3
Linear range		1-15	1-12	1-15	1-12
Mean		99.66	101.17	101.57	101.14
RMSE		0.12	0.085	0.11	0.086
RSD(%)		1.49	1.75	1.40	1.78
R^2		0.9993	0.9996	0.9997	0.9996
LOD		0.228	0.259	0.216	0.243

Table 6. Assay results of the accuracy and precision of the EXRSM and SRSM methods.

Added (µg/mL)		Found by EXRSM (µg/mL)		Found by SRSM (µg/mL)	
CT	**HQ**	**CT**	**HQ**	**CT**	**HQ**
1.00	3.00	1.01 (±0.02)[a]	3.05 (±0.08)	0.99 (±0.01)	2.97 (±0.09)
3.00	9.00	2.99 (±0.02)	8.94 (±0.05)	3.00 (±0.01)	9.09 (±0.13)
15.00	5.00	15.02 (±0.05)	5.07 (±0.08)	15.05 (±0.01)	4.98 (±0.02)
2.00	2.00	1.99 (±0.01)	2.00 (±0.01)	1.99 (±0.01)	2.02 (±0.02)

a: Standard deviation (n = 5).

Table 7. Assay results of the accuracy and precision of the PCR and PLS methods.

Added (µg/mL)		Found by PCR (µg/mL)		Found by PLS (µg/mL)	
CT	**HQ**	**CT**	**HQ**	**CT**	**HQ**
1.00	3.00	1.03 (±0.05)a	2.96 (±0.09)	1.03 (±0.07)	3.02 (±0.04)
3.00	9.00	2.95 (±0.08)	8.93 (±0.14)	2.94 (±0.11)	8.97 (±0.13)
15.00	5.00	15.03 (±0.11)	4.95 (±0.12)	15.05 (±0.07)	4.93 (±0.09)
2.00	2.00	2.05 (±0.13)	1.93 (±0.14)	2.07(±0.08)	1.94 (±0.007)

a: Standard deviation (n = 5)

Table 8. Results of the interference of different species in the simultaneous determination of CT and HQ in their binary mixture containing 2.0 µg mL^{-1} of each CT and HQ by the EXRSM and SRSM methods.

Species studied in HQ determination	Species studied in CT determination	Tolerance limit (WSpecies/WHQ or WCT)
K^+, Na^+, NH_4^+, Cl^-, Mg^{2+}, F^- Ca^{2+},Ni^{2+}, Br^-, EDTA, SO_4^{2-}	K^+, Na^+, NH_4^+, Cl^-, Mg^{2+}, F^- Ca^{2+},Ni^{2+}, Br^-, EDTA, SO_4^{2-}	1000
Co^{2+}, Cu^{2+}, Zn^{2+}	Co^{2+}, Cu^{2+}, Zn^{2+}	400
Fe^{2+}, citric acid	Fe^{2+}, citric acid	200
NO_3^-	NO_3^-	50
Phenol, resorcinol	-	10
NO_2^-	Phenol, resorcinol, NO_2^-	1

Table 9. Results for the simultaneous determination of CT and HQ in tap water samples using novel spectrophotometric methods.

Added (μg mL^{-1})		Found by EXRSM (μg mL^{-1})		Found by SRSM (μg mL^{-1})	
CT	HQ	CT	HQ	CT	HQ
2.00	5.00	2.00 (±0.02)	5.08(±0.07)	2.01(±0.02)	5.12 (±0.07)
3.00	6.00	3.01(±0.05)	6.06(±0.06)	3.00(±0.02)	6.04 (±0.02)
4.00	7.00	4.00 (±0.02)	7.06 (±0.05)	4.01(±0.03)	7.10 (±0.09)
5.00	8.00	5.00 (±0.05)	8.00(±0.02)	5.05 (±0.05)	8.08 (±0.11)
6.00	9.00	6.00 (±0.02)	9.00(±0.05)	6.00(±0.03)	8.94 (±0.06)
7.00	1.00	7.10 (±0.07)	1.00(±0.05)	7.07 (±0.06)	1.00 (±0.06)
1.00	2.00	0.99 (±0.05)	2.02 (±0.02)	0.95 (±0.05)	2.14 (±0.1)
2.00	1.00	2.00 (±0.07)	1.00 (±0.02)	2.00 (±0.06)	1.03 (±0.07)

Table 10. Results for the simultaneous determination of CT and HQ in tap water samples using the PCR and PLS methods..

Conc.		PCR		PLS	
CT	HQ	CT	HQ	CT	HQ
2.00	5.00	1.96 (±0.10)	4.82 (±0.17)	2.07 (±0.04)	4.83 (±0.13)
3.00	6.00	2.96 (±0.12)	5.92 (±0.09)	3.09 (±0.1)	5.97 (±0.06)
4.00	7.00	4.05 (±0.07)	6.84 (±0.18)	4.00 (±0.04)	6.93 (±0.06)
5.00	8.00	4.92 (±0.08)	7.82 (±0.13)	5.02 (±0.05)	8.03 (±0.06)
6.00	9.00	5.88 (±0.12)	8.76 (±0.11)	6.00 (±0.09)	9.02 (±0.09)
7.00	1.00	6.84 (±0.13)	1.06 (±0.14)	7.00 (±0.12)	1.01 (±0.12)
1.00	2.00	0.98 (±0.08)	2.08 (±0.98)	1.00 (±0.04)	2.00 (±0.04)
2.00	1.00	1.96 (±0. 16)	1.03 (±0.13)	2.04 (±0.06)	0.97 (±0.06)

Conclusion

Different simple, accurate, and selective univariate and multivariate spectrophotometric methods have been established and validated for the simultaneous determination of CT and HQ in laboratory prepared mixtures. These methods are fast and accurate, and do not require any toxic and expensive organic solvents.

As it is evident from the results the power of the novel univariate methods EXRSM and SRSM in the simultaneous determination of HQ and CT is comparable to that of the multivariate methods (such as PCR and PLS), which can be an advantage for these methods. In EXRSM and SRSM, unlike the PCR and PLS methods, there is no need for any computer program, and by simple mathematical equations, the concentration of each one of the isomers can be determined. The successful application of the two novel methods EXRSM and SRSM for the simultaneous determination of HQ and CT with different ratios in the tap water samples proved their good applicability.

Acknowledgment

The authors are thankful to the Shahrood University of Technology Research Council for the support of this work.

References

[1] L.A. Alshahrani, L. Liu, P. Sathishkumar, J. Nan, F.L. Gu, Journal of Electroanalytical Chemistry, 815 (2018) 68.

[2] M.A. Ghanem, Electrochemistry Communications, 9 (2007) 2501.

[3] C. Wang, R. Yuan, Y. Chai, F. Hu, Analytical Methods, 4 (2012) 1626.

[4] E.C. Figueiredo, C.R.T. Tarley, L.T. Kubota, S. Rath, M.A.Z. Arruda, Microchemical journal, 85 (2007) 290.

[5] Z. Yaoyu, T. Lin, Z. Guangming, Z. Yi, L. Zhen, L. Yuanyuan, C. Jun, Y. Guide, Z. Lu, Z. Sheng, Analytical Methods, 6 (2014) 2371.

[6] K.O. Lupetti, F.R. Rocha, O. Fatibello-Filho, Talanta, 62 (2004) 463.

[7] A. Afkhami, H. Khatami, Journal of Analytical Chemistry, 56 (2001) 429.

[8] H. Qiu, C. Luo, M. Sun, F. Lu, L. Fan, X. Li, Analytica Chimica Acta, 744 (2012) 75.

[9] S. Li, X. Li, J. Xu, X. Wei, Talanta, 75 (2008) 32.

[10] H. Cui, C. He, G. Zhao, Journal of Chromatography A, 855 (1999) 171.

[11] A. Asan, I. Isildak, Journal of Chromatography A, 988 (2003) 145.

[12] B. Lee, H. Ong, C. Shi, C. Ong, Journal of Chromatography B: Biomedical Sciences and Applications, 619 (1993) 259.

[13] M.F. Pistonesi, M.S. Di Nezio, M.E. Centurión, M.E. Palomeque, A.G. Lista, B.S.F. Band, Talanta, 69 (2006) 1265.

[14] B. Pranaityt, A. Padarauskas, A. Dikčius, R. Ragauskas, Analytica Chimica Acta, 507 (2004) 185.

[15] J.A. Garcia-Mesa, R. Mateos, Journal of agricultural and food chemistry, 55 (2007) 3863.

[16] M. Nazari, S. Kashanian, P. Moradipour, N. Maleki, Journal of Electroanalytical Chemistry, 812 (2018) 122.

[17] L.A. Goulart, R. Gonçalves, A.A. Correa, E.C. Pereira, L.H. Mascaro, Microchimica Acta, 185 (2018) 12.

[18] Y. Xiang, L. li, H. liu, Z. Shi, Y. Tan, C. Wu, Y. Liu, J. Wang, S. Zhang, Sensors and Actuators B: Chemical, 267 (2018) 302.

[19] H. Wang, Q. Hu, Y. Meng, Z. Jin, Z. Fang, Q. Fu, W. Gao, L. Xu, Y. Song, F. Lu, Journal of hazardous materials, 353 (2018) 151.

[20] M. Ghaedi, S. Hajati, B. Barazesh, F. Karimi, G. Ghezelbash, Journal of Industrial and Engineering Chemistry, 19 (2013) 227.

[21] H.M. Lotfy, S.S. Saleh, N.Y. Hassan, S.M. Elgizawy, Analytical Chemistry Letters, 3 (2013) 70.

[22] H.M. Lotfy, M.A.-M. Hagazy, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 96 (2012) 259.

[23] H.M. Lotfy, M.A.M. Hegazy, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 113 (2013) 107.

[24] A. Parmar, S. Sharma, TrAC Trends in Analytical Chemistry, 77 (2016) 44.

[25] C.B. Ojeda, F.S. Rojas, Microchemical Journal, 106 (2013) 1.

[26] K.R. Beebe, R.J. Pell, M.B. Seasholtz, Chemometrics: a practical guide, Wiley-Interscience, 1998.

[27] R. Rosipal, N. Krämer, Overview and recent advances in partial least squares, in: Subspace, latent structure and feature selection, Springer, 2006, pp. 34-51.

[28] J.P.A. Martins, R.F. Teofilo, M. Ferreira, Journal of Chemometrics, 24 (2010) 320.

[29] G. Bagherian, M. A. Chamjangali, H. Eskandari, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 67 (2007) 378.

[30] M .F. Abdel-Ghany, L. A. Hussein, M. F. Ayad, M. M. Youssef, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 171 (2017) 236.

[31] S. M. Tawakkol, M. Farouk, O. A. Elaziz, A. Hemdan, M. A. Shehata, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 133 (2014) 300.

[32] M. A. Chamjangali, G. Bagherian, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 62 (2005) 189.

How to cite this manuscript: Ghadamali Bagherian*, Fatame Salehi Mobarake, Mansour Arab Chamjangali, Motahare Ashrafi, Haniye Borzooei, Comparison between univariate and multivariate calibration methods for simultaneous spectrophotometric determination of catechol and hydroquinone in their binary mixture. Frontiers in Chemical Research, 2020, 2, 1-9. doi: 10.22034/FCR.2020.116897.1011