RESEARCH PAPER

A rapid spectrophotometric method for simultaneous determination of catechol, hydroquinone, and resorcinol in water samples using mean centering spectra

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Abstract

A simple and sensitive spectrophotometric method was developed for determination of ternary mixtures catechol (CT), hydroquinone (HQ) and resorcinol (RS) without previous separation. The method is based on mean centering of second ratio spectra. The mathematical explanation of the procedure is illustrated. The method was evaluated by determination CT, HQ and RS in synthetic ternary mixtures. The procedure was successfully applied to the simultaneous determination of these analytes in water samples.

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Introduction

The isomers of dihydroxybenzene catechol (1,2-dihydroxybenzene,CT), hydroquinone (1,4-dihydroxybenzene, HQ) and resorcinol (1,3-dihydroxybenzene, RS) are widely usedin medicines, pesticides, cosmetics, tanning, flavoring agents, antioxidants, dyes, and photography chemicals (Wang *et al.*, 2003, Ahammad *et al.*, 2011). They are also important indicators for environmental monitoring (Zhao *et al.*, 2009, Sys *et al.*, 2013). Because of the high toxicity and low degradability of HQ, CC and RC in ecological environment, they are considered as environmental pollutants by the Environmental Protection Agency (EPA) and the European Union (EU) (Wang *et al.*, 2007).

As environmental pollutants in the ecological system, it is very important to develop simple and rapid analytical methods for determination of HQ, CC and RC. Because of their similar chemical structure and difficulty in separation and detection simultaneously, it is important to develop simple, rapid, and efficient methods to simultaneously monitor trace dihydroxybenzene isomers. Up to now, many analytical methods have been established to determine dihydroxybenzene isomers, such as high performance liquid chromatography (Marrubini *et al.*, 2005), fluorescence (Lin *et al.*, 2010, Pistonesi *et al.*, 2006), chemiluminescence (Cui *et al.*, 2006).

Spectrophotometer (Nagaraja *et al.*, 2001,Afkhami *et al.*, 2001), gas chromatography/mass spectrometry (Moldoveanu *et al.*, 2007), capillary electro chromatography (Guan *et al.*, 2000) and electrochemical methods (Li *et al.*, 2010, Ahammad *et al.*, 2011, Yu *et al.*, 2009, Zhou *et al.*, 2013, Feng *et al.*, 2013). Compared with other analytical strategies, Spectrophotometer methods are very simple, fast and inexpensive for the various analysis, but have low selectivity and sensitivity. Spectroscopic interferences can be a problem when working with real samples and so many published methods require the incorporation of some sort of separation/extraction methodology prior to analysis.

A new spectrophotometer method for the analysis of binary and ternary mixtures, without prior separation steps called "mean centering of ratio spectra" method was developed (Bahram *et al.*, 2007, Madrakian *et al.*, 2007, Afkhami *et al.*, 2006, Afkhami *et al.*, 2005). This method is based on the successive derivatives of ratio spectra in two steps (Madrakian *et al.*, 2008, Kamyabi *et al.*, 2009, Chamsaz *et al.*, 2010). To explain the mean centering expression, let us consider a mixture of three compounds *X*, *Y* and *Z*. If there is no interaction among the compounds and Beer's low is obeyed for each compound, it can be written:

$$A = \alpha_W C_W + \alpha_X C_X + \alpha_Y C_Y \quad (1).$$

Where *A* is the vector of the absorbance of the mixture, α_W, α_X and α_Y are the molar absorptivity vectors of *W*, *X* and *Y* and C_W, C_X and C_Y are the concentrations of *W*, *X* and *Y*, respectively. If Eq. (1) is divided by α_Y corresponding to the spectrum of a standard solution of *Y* in ternary mixture, the first ratio spectrum is obtained in the form of Eq. (2) (for possibility of dividing operation, the zero values of α_Z should not be used in the divisor):

$$B = \frac{A}{\alpha_Y} = \frac{\alpha_W C_W}{\alpha_Y} + \frac{\alpha_X C_X}{\alpha_Y} + C_Y \quad (2)$$

If the Eq. (2) is mean centered (MC), since the mean centering of a constant (C_Z) is zero, Eq. (3) would be obtained:

$$MC(B) = MC\left[\frac{\alpha_W C_W}{\alpha_Y}\right] + MC\left[\frac{\alpha_X C_X}{\alpha_Y}\right] \quad (3)$$

By dividing Eq. (3) by $MC\left[\frac{\alpha_X}{\alpha_Y}\right]$, corresponding to the mean centering of the ratio of the spectra of the standard solutions of *X* and *Y* the second ratio spectrum is obtained as Eq. (4) (for possibility of dividing operation, the zero values of $MC\left[\frac{\alpha_X}{\alpha_Y}\right]$ should not be used in the divisor):

$$D = \frac{MC(B)}{MC(\frac{\alpha_X}{\alpha_Y})} = \frac{MC[\alpha_W C_W/\alpha_Y]}{MC\left[\frac{\alpha_X}{\alpha_Y}\right]} + C_X \quad (4)$$

Now if the Eq. (4) is mean centered, since the mean centering of a constant (C_X) is zero, Eq. (5) would be obtained:

$$MC(D) = MC\left[\frac{MC[\alpha_W C_W/\alpha_Y]}{MC(\frac{\alpha_X}{\alpha_Y})}\right] \quad (5)$$

Eq. (5) is the mathematical foundation of multi-component analysis that permits the determination of concentration of each of the active compounds in the solution (*W* in this equation) without interfering from the other compounds of the ternary system (*X* and *Y* in these equations).

As Eq. (5) shows there is a linear relation between the amount of MC(*D*) and the concentration of *W* in the solution. A calibration curve could be constructed by plotting MC(*D*) against concentration of *W* in the standard solutions of *W* or in the standard ternary mixtures. For more sensitivity the amount of MC(*D*) corresponding to maximum or minimum wavelength should be measured.

Calibration graphs for *X* and *Y* could also be constructed as described for W. In this study, Mean Centering Spectra Spectrophotometer Method was described for the simultaneous determination of Catechol, Hydroquinone, and Resorcinol.

Some synthetic samples including different concentration ratios of these isomers had been analyzed with good agreement without prior separation and applied to the determination of Catechol, Hydroquinone, and Resorcinol in water samples.

Materials and methods

Materials

All chemicals were of analytical reagent grade. Stock solutions (100 mgL⁻¹) of catechol (W), resorcinol (X) and hydroquinone (Y) were prepared by direct dissolution of proper amounts of chemicals from Merck (Darmstadt, Germany) in deionized doubly distilled water. Standard solutions of each catechol, hydroquinone and resorcinol for binary and ternary mixture analysis were obtained by appropriate dilution of the stock solutions.

Procedure

After the preparation of stock solutions of catechol, resorcinol and hydroquinone, Portions of three solutions were separately diluted with deionized doubly distilled water to attain the linear ranges. The absorption spectra of the prepared standard solutions were recorded in the range of 250–320 nm against deionized doubly distilled water on a Shimadzu UV-1800 scanning spectrophotometer using 1 cm quartz cells. The absorption spectra of the synthetic mixtures specified in Table 1 were recorded after the preparation of solutions by mixing stock solutions of the isomers with in suitable proportions. All calculations in the computing process were done in Microsoft Excel for Windows.

Table. 1. Results for several experiments for analysis of catechol, hydroquinone and resorcinol in ternary mixtures in different concentration ratios by proposed method.

|	Composition of synthetic mixture			Predicted concentration		
	Catechol	Resorcinol	Hydroquinone	Catechol	Resorcinol	Hydroquinone
1	20	5	6	19.02	5.14	7.12
2	5	5	22	6.50	4.14	20.87
3	7	10	6	7.84	11.55	8.01
4	5	20	12	4.38	21.11	11.63
5	7	20	22	8.11	19.23	21.14
6	5	10	22	6.12	10.25	21.36
7	5	5	12	5.52	5.36	11.89
8	20	10	12	21.11	9.42	11.36
9	7	5	6	8.17	6.21	5.02
10	5	5	6	5.37	4.65	5.41

Results and discussion

The structure of the catechol, resorcinol and hydroquinone are shown in Fig. 1. In this work, the linear range for catechol, hydroquinone and resorcinol was checked and the Beer's law was obeyed in the concentration ranges 3–24μg mL⁻¹,

5–25μg mL⁻¹ and 3–24μg mL⁻¹, respectively. As Fig. 2 shows, the zero order absorption spectra of catechol, hydroquinone and resorcinol overlapped in the wavelength region of 250–320nm that did not allow direct spectrophotometer determination of each of them separately and there need to be separated which is a time consuming step.

So, the aim of this work was to develop simple and accurate spectrophotometer method for the determination of catechol, hydroquinone and resorcinol ternary mixtures with asimple mean centering method without previous separation.
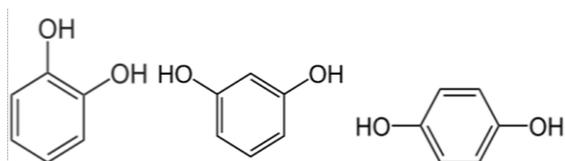
**Fig. 1.** Structure of Catechol (a), resorcinol (b) and hydroquinone (c).
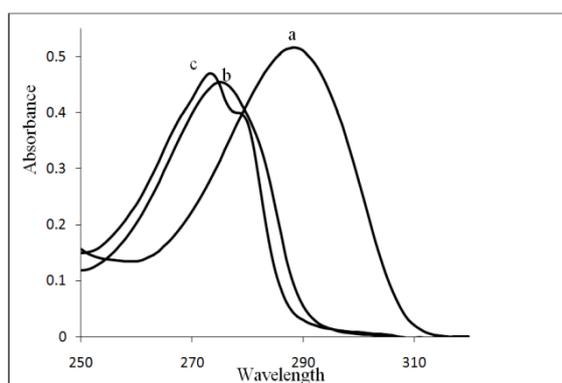
Fig. 2. The zero order spectra of Catechol (a), hydroquinone (b) and resorcinol (c).

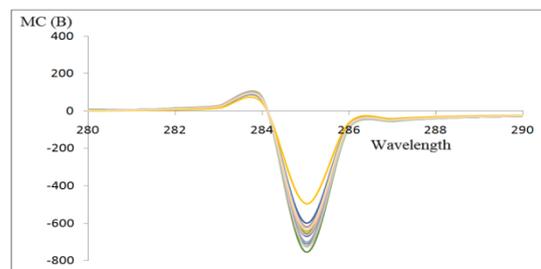*Spectrophotometer determination of catechol*

For determination of catechol (W), the absorption spectra of the mixture solutions of the catechol (W), hydroquinone (Y) and resorcinol (X) with different concentrations were recorded in the wavelength range of 250–320 nm (Fig 3a) and divided by the normalized spectrum of hydroquinone (Y) and the ratio spectra B according to Eq. 2 were obtained. Mean centering (MC(B)) of the ratio spectra was obtained (Fig 3b).

Then the absorption spectra of the mixture solutions of the resorcinol and hydroquinone with different concentrations were recorded in the wavelength range of 280–290nm and divided by the normalized spectrum of hydroquinone (Y) and the ratio spectra were obtained. Mean centering ($MC\left[\frac{\alpha_X}{\alpha_Y}\right]$) of the ratio spectra was obtained (Fig 3c). After that, $MC(B)$ are divided by $MC\left[\frac{\alpha_X}{\alpha_Y}\right]$ corresponding to the mean
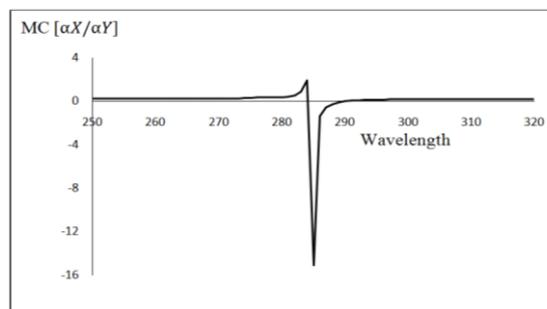
centering of the ratio of the spectra of X and Y and therefore, second ratio spectra according to Eq. (4) were obtained. Mean centering of these vectors was obtained (Fig 3d). The concentration of catechol (W) was determined by measuring the amplitude of the resulting spectra at 290 nm corresponding to the maximum wavelength.
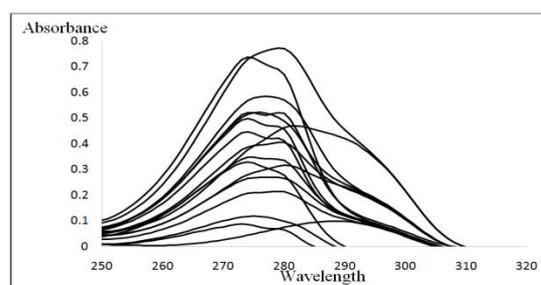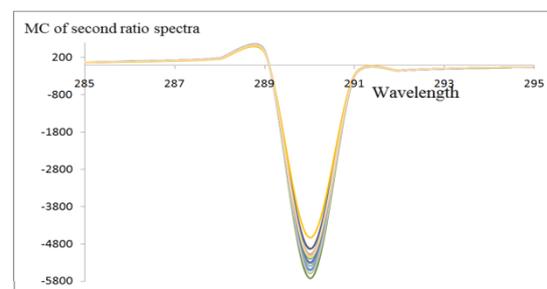

Fig. 3a.

Fig. 3b.

Fig. 3c.

Fig. 3d.

Fig. 3. The spectra of randomly selected mixtures of the catechol, resorcinol and hydroquinone (a) the Mean centering (MC(B)) of the ratio spectra (b) Mean centering ($MC\left[\frac{\alpha_X}{\alpha_Y}\right]$) of the ratio spectra (c) and the second ratio spectra for determination of catechol (d).

Spectrophotometer determination of resorcinol

For determination of resorcinol (X), the absorption spectra of the mixture solutions of the catechol (W), hydroquinone (Y) and resorcinol (X) with different concentrations were recorded in the wavelength range of 250–320 nm (Fig 3a) and divided by the normalized spectrum of hydroquinone (Y) and the ratio spectra B were obtained. Mean centering of the ratio spectra was obtained (Fig 4a). Then the absorption spectra of the mixture solutions of the catechol (W) and hydroquinone (X) with different concentrations were recorded in the wavelength range of 280–290nm and divided by the normalized spectrum of hydroquinone (Y) and the ratio spectra were obtained. Mean centering ($MC\left[\frac{\alpha_W}{\alpha_Y}\right]$) of the ratio spectra was obtained (Fig 4b). After that, MC are divided by $MC\left[\frac{\alpha_W}{\alpha_Y}\right]$ corresponding to the mean centering of the ratio of the spectra of W and Y and therefore, second ratio spectra were obtained. Mean centering of these vectors was obtained (Fig 4c). The concentration of resorcinol (X) was determined by measuring the amplitude of the resulting spectra at 300 nm corresponding to the maximum wavelength.
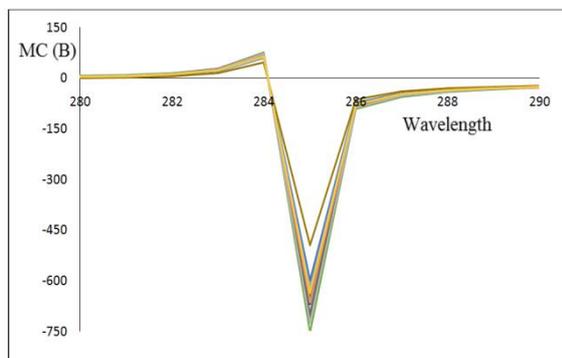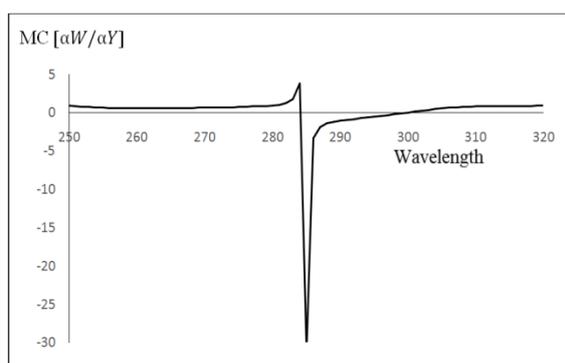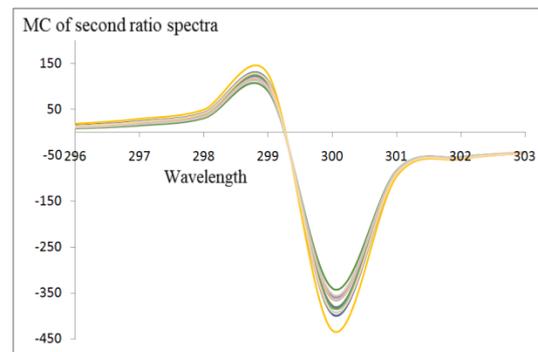

Fig. 4c.

Fig. 4. The Mean centering (MC(B)) of the ratio spectra (a) Mean centering ($MC\left[\frac{\alpha_W}{\alpha_Y}\right]$) of the ratio spectra (b) and the second ratio spectra for determination of resorcinol (c).

Spectrophotometer determination of hydroquinone

For determination of hydroquinone (Y), the absorption spectra of the mixture solutions of the catechol (W), hydroquinone (Y) and resorcinol (X).

With different concentrations were recorded in the wavelength range of 250–320nm (Fig 3a) and divided by the normalized spectrum of resorcinol (X) and the ratio spectra B were obtained. Mean centering of the ratio spectra was obtained (Fig. 5a).

Then the absorption spectra of the mixture solutions of the catechol (W) and resorcinol (X) with different concentrations were recorded in the wavelength range of 280–290nm and divided by the normalized spectrum of resorcinol (X) and the ratio spectra were obtained.

Mean centering ($MC\left[\frac{\alpha_W}{\alpha_X}\right]$) of the ratio spectra was obtained (Fig. 5b). After that, MC are divided by $MC\left[\frac{\alpha_W}{\alpha_x}\right]$ corresponding to the mean centering of the ratio of the spectra of W and X and therefore, second ratio spectra were obtained. Mean centering of these vectors was obtained (Fig. 5c).

The concentration of hydroquinone (Y) was determined by measuring the amplitude of the resulting spectra at 259 nm corresponding to the maximum wavelength shown in Fig. 5c.
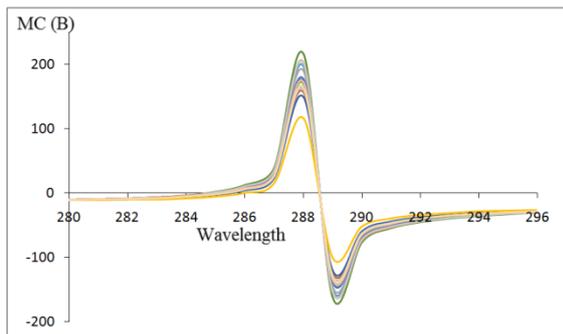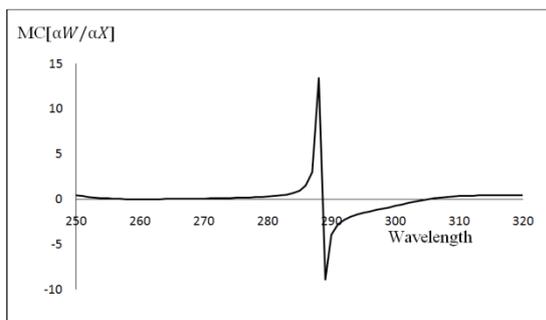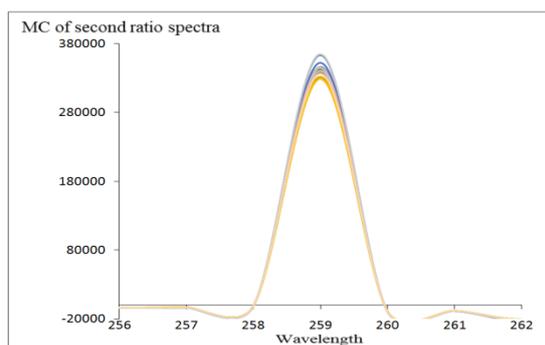

Fig. 4a.

Fig. 4b.

Fig. 5a.

Fig. 5b.

Fig. 5c.

Fig. 5. The Mean centering (MC(B)) of the ratio spectra (a) Mean centering ($MC\left[\dfrac{\alpha_W}{\alpha_X}\right]$) of the ratio spectra (b)

and the second ratio spectra for determination of hydroquinone (c).

Analysis of synthetic mixtures
To evaluate of the method, several synthetic mixtures with different concentration ratios of catechol, hydroquinone and resorcinol were analyzed using the simple UV–Vis method. The results are given in Table 1. As can be seen, the model was successful for the prediction of the concentration of dihydroxybenzene isomers.

Application
To investigate the performance of the novel analytical method for the simultaneous determination, experiments were performed to determine the concentration of dihydroxybenzene isomers in tap water samples. Because the content of dihydroxybenzene isomers in tap water was very low, the samples were spiked with 5m Mcatechol, 5m Mhydroquinone, and 3m Mresorcinol.

The contents of isomers were detected using the standard addition method, and the results are listed in Table 2. As result show, mean centering of ratio spectra method is very useful for resolving ternary mixtures in the complex samples.

The values of recovery are in the range from 96.3 to 104.6%, suggesting that the method is very accurate.

Table 2. Results of analysis of catechol, hydroquinone and resorcinol in water sample by the proposed method.

	Tap water			River water		
	Catechol	Resorcinol	Hydroquinone	Catechol	Resorcinol	Hydroquinone
Spiked (mM)	5	3	5	5	3	5
Found (mM)	5.5	3.7	5.2	5.7	3.8	5.8
RSD (%)	3	2.2	3.2	3.7	3.1	3.8
Recovery (%)	103.3	102.7	98.2	104.6	96.3	97.8

Conclusion
The proposed method for the resolving of ternary mixtures of catechol, hydroquinone and resorcinol is simple, very sensitive and easy to understand and apply. The method can also be applied for analysis of real samples such as tap water samples.

Spectrophotometer methods can be regarded as a useful alternative to chromatographic techniques in the routine quality control analysis of pharmaceutical formulations allowing rapid determination at relatively low cost.

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