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Wavelength region selection and spectrophotometric simultaneous determination of naphthol isomers based on net analyte signal

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Abstract

Naphthol isomers were simultaneously and spectrophotometrically determined in wastewater, using a model based on net analyte signal (NAS). The calibration method used is a variation of the original hybrid linear analysis method as proposed by Goicoechea and Olivieri (HLA/GO). Owing to spectral interferences, the simultaneous determination of mixtures of naphthol isomers, using a spectrophotometric method, is difficult. A rapid and powerful method was used for wavelength selection in the modeling step, based on the minimization of the error indicator (EI), which was estimated as a function of the moving spectral region. The calculation of the net analytical signal using a modified HLA/GO method allows us to determine several figures of merit, as selectivity, sensitivity, analytical sensitivity and limit of detection of the proposed multivariate calibration. The limit of detection (LOD) for 1 and 2-naphthol were 0.04 and 0.06 (µg/mL) respectively. The proposed model was tested in the analysis of wastewater samples, without previous sample preparation steps, obtaining recovery values between 98 and 104.00%, for 1-naphthol and between 97.00 and 103.00%, for 2-naphthol.

Keywords: Wavelength selection; hybrid linear analysis; naphthol isomers; wastewater; spectrophotometric.

Introduction

In recent years, there has been a significant interest in the determination of petroleum hydrocarbons pollutants in air, soil, and water samples. Noticeable amounts of petroleum compounds are emptied into the environment as industrial effluents. They are considered as one of the contaminants of soil and groundwater owing to their leakage during storage and racking by forwarding lines or careless handling and accidents [1-5]. Phenolic compounds are the most toxic contaminants in wastewater, owing to their wide application in various industrial processes, such as refineries, coking operations, coal processing, pharmaceutical, pulp and paper industries, and the manufacture of petrochemicals. Owing to their high toxicity and persistence in the environment, both the US Environmental Protection Agency (EPA) and the European Union have included some of the phenols in their list as great preference pollutants [6]. The nature of petroleum hydrocarbon

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pollution is highly variable and contains complex matrix [7]. A variety of analytical methods have been described in papers for the determination of naphthols; these methods include capillary zone electrophoresis [8], flow-through fluorimetry [9], HNMR [10], electrochemical [11], high-pressure liquid chromatography (HPLC) [12], gas chromatography-mass spectrometry (GC-MS) [13], fluorescence spectroscopy [14], and Fourier transform infrared spectroscopy (FTIR) [15]. Sometimes, GC methods require relative reagents, beneficiation and derivatization before analysis and it cannot be directly used for aqueous samples. Despite the excellent sensitivity of electrochemical methods, they suffer from low values selectivity. HPLC and capillary electrophoresis methods are better alternative methods for hazardous organic solvents and produce waste with a high percentage of organic solvents [16]. Spectrophotometric methods [17] are the most popularly used methods due to common availability of instrumentation, wide application range, experimental speed, cost-effective, precision and accuracy of the technique [18]. The HLA/GO and HLA/Xu, Schechter (X/S), and a new family of multivariate calibration methods based on the concept of net analyte signal (NAS) were offered by Lorber [21] and explained by Berger *et al.* [22]. The proposed method was presented based on the concept of NAS by HLA/XS [21] and HLA/GO [22]. Unlike the method used, X/S and HLA/GO selected the optimum number of factors using the cross validation methods of Haaland and Thomas [23-24]. The multivariate NAS was defined by Ferre *et al.* as the part of the impure signal of the mixture spectrum that is effective for prediction. By applying NAS, the contribution of the pure component of interest is eliminated from the data matrix [25]. NAS calculations [26] allow the estimation of the figures of merit of an analytical method, such as the detection of limit, sensitivity, selectivity, and also selecting optimum wavelength ranges for analysis. NAS-based wavelength selection may be performed by combining net analyte signal regression plot (NASRP) for each new prediction sample with a minimum error indicator (EI) value which shows the spectral region where the effect of the spectral interferences is minimized [27,28]. As shown subsequently, a very strong degree of spectral overlap exists in the spectral region of interest between naphthol isomers and the normal wastewater sample absorption spectrum. Based on these overlapping peaks, the problem of these isomers in the wastewater samples was determined simultaneously. This study reports on the possibility of quantifying naphthol isomers in a wastewater sample using spectrophotometric determination with calibration based on HLA/GO.

Experimental

Materials and methods

The wastewater samples used in this study were collected from Shazand Petrochemical Corporation (Arak, Iran). Particles were removed from this wastewater sample using a filter paper. Naphthol isomers, acetic acid, phosphoric acid, boric acid, and sodium hydroxide were purchased from Merck. Standard stock solutions of 1 and 2-naphthol were prepared by dissolving appropriate amounts of their corresponding compounds in methanol. Working standard solutions at different concentrations were freshly prepared by mixing the appropriate volumes of the stock solutions and diluting with

deionized water. In this study, the pH values of the working solution was adjusted using universal buffers (acetic acid, acid-phosphoric, boric-acid mixture) [29]. Wastewater samples were constructed by spiking blank waste with appropriate amounts of the standard solutions of naphthols and buffer solution.

Instrumentation and software

A Cary 300 spectrophotometer controlled by a computer and equipped with a 1-cm path length quartz cell was used for UV spectra acquisition. The spectra were acquired between 2۰0 and 350 nm (1 nm resolution). A Metrohm 692 pH-meter furnished with a combined glass-saturated calomel electrode was calibrated with at least two buffer solutions at pH 3.00 and 9.00. The program for HLA calculation was written in MATLAB Version 7.8.0 (R2009a) and run on a VAIO Personal Computer (4GB RAM) equipped with the Windows 8 operating system.

Calibration and prediction sets

Wastewater samples from Shazand Petrochemical Corporation were used for calibration and prediction. The calibration set was designed with 16 diluted wastewater pool samples (2 mL/10 mL) with 1-naphthol added in the range of 1.00 to 8.00 (µg/mL) and 2-naphthol in the range of 1.00 to 16.00 (µg/mL). A prediction set consists of diluted wastewater pool samples (2 mL/10 mL) with 1-naphthol added in the range of 1.50 to 7.50 (µg/mL) and 2-naphthol in the range of 2.00 to 12.00 (µg/mL).

Proposed procedure for the analysis of 1 and 2-naphthol in wastewater samples

The appropriate amounts of standard solutions of naphthol isomers were added to 2.0 mL of the wastewater sample, 5 mL of the universal buffer solution (0.04 M) was added, and each sample was diluted to 10 mL with deionized water in order to obtain the desired concentration. The absorption spectrum was recorded in the region between 200 and 350 nm, digitized at every 1 nm, against a solution containing the same amount of buffer solution. The spectral data were analyzed using the optimized HLA/GO calibration model, using 2 optimized factors, and a range of wavelengths between 270 and 320 nm.

Results and discussion

Optimization of experimental condition

To find the best condition, the influence of pH values on the spectrum of 1 and 2-naphthol at a constant concentration of each naphthol was studied. In order to select the optimal pH value at which the minimum spectral overlap occurred, the influence of pH on the absorption spectra of isomers were studied over the pH range of 2.00 to 12.00. At the pH range of 7.00 to 12.00, the absorbance almost remained unchanged. However, pH 7.00 was chosen as the optimum pH for this work, because both isomers recorded maximum absorbance and least overlap at this pH. To overcome the problem of spectral overlaps, a suitable and simple technique, HLA/GO, which presents a good recovery is used. The spectra, a mixture of naphthol isomers solution between 200 and 350 nm wavelengths by 1-nm intervals were recorded and then the data were digitized and stored for later treatment. In wavelength lower than 300 nm, the wastewater sample shows a very high absorption and a high absorption also occurs for higher wavelengths with an absorption maximum located around 324 nm. In the presence of isomers, the wavelength range, useful for the analysis, appears to be between 250 and 340 nm. However, in this range, a strong spectral overlap between naphthol

isomers and the wastewater sample may also be observed as shown in Figure 1. With the objective of carrying out the simultaneous analysis of these isomers in the wastewater sample without previous sample preparation steps, a calibration set has been designed containing this waste as interference. Also, a selection of the optimum range of wavelengths, was made based on the NAS analysis.

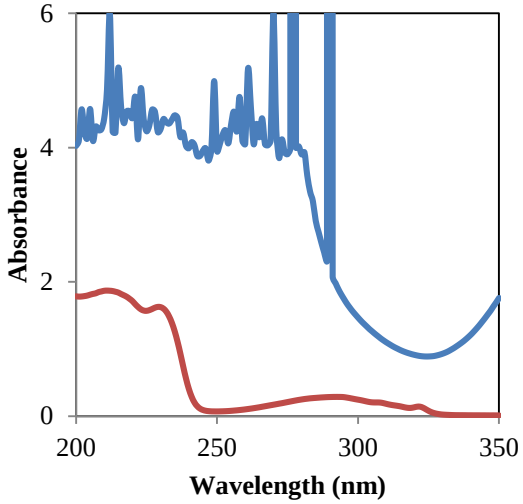

Figure 1. Absorption spectrum of a wastewater undiluted; Absorption spectrum sample diluted (2 mL/10 mL).

Experimental design of the calibration matrix

A mixture design was used to statistically maximize the information content in the spectra [30]. A calibration set of 16 and prediction set containing 6 samples were taken. A linear range (LR) of calibration graphs were determined for 1 and 2-naphthol between 1.00 to 14.00 and 1.00 to 16.00 (µg/mL) variables, respectively. Table 1 summarizes the composition of the binary mixtures used in the calibration matrices and a diagrammatic representation of the mixture design for the prediction set. Six mixtures not included in the previous set were employed as an independent test. The volume of the wastewater sample prepared was fixed at 2.00 mL in a final volume of 10 mL of the calibration or prediction samples.

Table 1. Composition of calibration and prediction sets

Mixture number	Concentration (µg/mL)		Mixture number	Concentration (µg/mL)		Mixture number	Concentration (µg/mL)	
	1-Naphthol	2-Naphthol		1-Naphthol	2-Naphthol		1-Naphthol	2-Naphthol
M1	1	1	M9	5	1	P.s		
M2	1	6	M10	5	6	M1	1.5	4.5
M3	1	11	M11	5	11	M2	2	2
M4	1	16	M12	5	16	M3	2	8
M5	3	1	M13	8	1	M4	7.5	5.5
M6	3	6	M14	8	6	M5	6	12
M7	3	11	M15	8	11	M6	7	3
M8	3	16	M16	8	16			

P.s: Prediction set

[a]The volume of wastewater was fixed in 2.0 mL in a final volume of 10 mL of calibration or prediction sample

Wavelength selection

In the present work, the chosen optimal factor number was 2 using the method of cross-validation for algorithm HLA in the range of 250 to 340 nm. Then, using the optimized number of factors selected in this region, an EI was estimated for each prediction sample, using the information of the NASRP, which corresponds to the r* vs. s* plot, where r* is the norm of the net analyte spectrum in the prediction sample and s* is the norm of the spectrum of the *i* pure analyte. The expression for EI, as applied in this study is [28]:

$$EI = \frac{\sqrt{\left[S^2\left(1+\frac{N^2S^2}{4\|r^*\|^2}\right)\right]}}{\|r^*\|} \quad (1)$$

Where S is the standard deviation from the best fitted straight line to the NASRP (in a certain spectral region) and N is the number of points in the second plot. A search for the minimum EI includes calibration, calculation of the cross-validation value of the optimum calibration factor number, and computation of r* and s* for each estimated spectral region. In each spectral region, the optimum numbers of factors values for each region were applied for calibration and calculation of EI. The best found values for the prediction samples and the least EI values permit us to choose a favorable wavelength range for the HLA analysis [31]. In Table 2, the ranges of wavelengths were tested, the EI values estimated, and the predicted values for two test samples have been summarized. The EI values increase when the wavelength range is near the background absorption of wastewater (absorption wavelength shorter than 250 nm) and decrease for higher wavelengths. Nevertheless, the use of wavelengths higher than about 320 nm does not appear to be useful. The least EI corresponds with the range between 270 and 320 nm for both components. Figure 2(a) shows NAS vectors vs. wavelength number. Once the NAS for a given prediction sample has been calculated, its NASRP can be constructed by plotting the elements of r* as a function of those of s*. Notice that the concentration C_i is the best fitted slope (mean centered) of the NASRP (forced to have zero intercept). The better consent was acquired in the region between 270 and 320 nm. Figure 2(b) presents the NASRP obtained for a prediction sample in the optimum wavelength range. The theoretical and found concentrations calculated from the slope of the NASRP plots are shown in the caption of the figure, respectively.

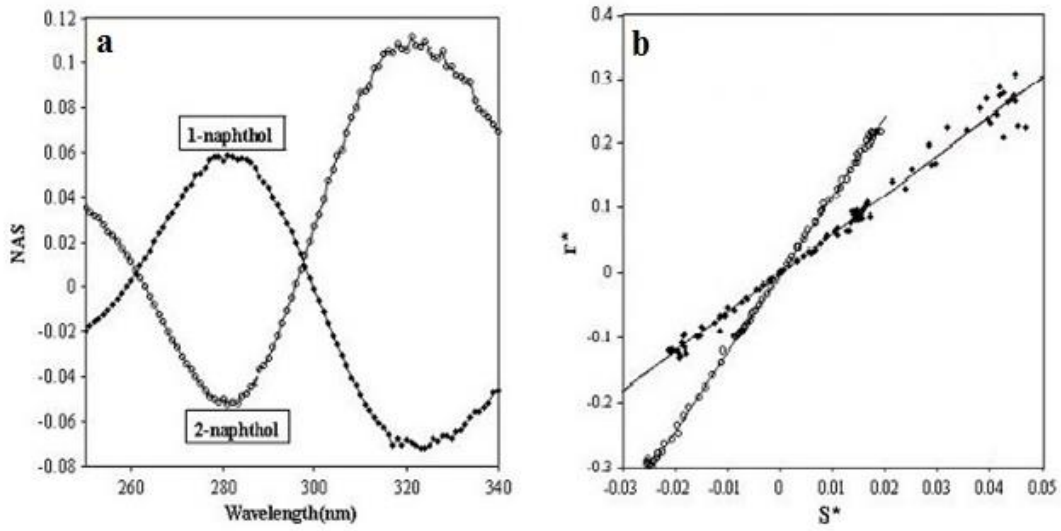

Figure 2. (a) NAS vectors to a wastewater sample containing 6.00 (µg/ mL) of 1-naphthol and 12.00 (µg/mL) of 2-naphthol; (b) r* vs. S* plot in the region of the minimum EI.

Table 2. Selection of the wavelength range in the prediction of 1 and 2-naphthol in wastewater sample by application of the NAS signal and assessment of the EI

Sample	Content	Sensor range	1-naphthol			2-naphthol		
			EI	Actual (µg/mL)	Found (µg/mL)	EI	Actual (µg/mL)	Found (µg/mL)
1	Wastewater sample 2ml/10ml	250-340	0.026	6	6.160	0.068	12	12.360
	1-and 2-naphthol	270-320	0.003		6.050	0.004		12.050
2	Wastewater sample 2ml/10ml	250-340	0.041	2	2.053	0.041	2	2.120
	1-and 2-naphthol	270-320	0.036		2.003	0.036		2.010

The number of factors used for prediction is 2.

Statistical parameters for the optimized HLA/GO model

The predicted concentrations of the calibration samples were estimated and compared with the actual concentrations and prediction error of the squares:

$$\mathrm{PRESS} = \sum \left(C_{act} - C_{pred} \right)^2 \qquad (2)$$

This was fixed using two factors for both components. The criterion explained by Haaland and Thomas was used to optimize the number of factors. Usual statistical parameters were used, such as REP:

$$\mathrm{REP} = \left(\frac{100}{\bar{C}} \right) \left[\left(1/I \right) \sum_{1}^{I} \left(C_{act} - C_{pred} \right)^2 \right]^{1/2} \qquad (3)$$

And the square of the correlation coefficient (R^2):

$$R^2 = 1 - \sum_{1}^{I} \left(C_{act} - C_{pred} \right)^2 \Big/ \sum_{1}^{I} \left(C_{act} - \bar{C} \right) \qquad (4)$$

Where $\bar{C}$ is the average component concentration in the i calibration mixtures and was also calculated [23]. To verify the predictive ability of these models, the RMSEP and RSEP can be used (Table 5).

$$RMSEP = \sqrt{\frac{\sum_{1}^{n} \left(y_{pred} - y_{obs} \right)^2}{n}} \qquad (5)$$

$$RSEP(\%) = \sqrt{\frac{\sum_{i=1}^{n}\left(y_{pred} - y_{obs}\right)^2}{\sum\left(y_{obs}\right)^2}} \quad (6)$$

Where y_{pred} is the predicted concentration, y_{obs} observed value of the sample, and n is the number of samples in the validation set. Despite the similar statistical parameters and figures of merit observed for both compounds, the most desired value was recorded for 2-naphthol. The proposed model was tested in the analysis of prediction (Table 3).

Table 3. Actual and found results of wastewater sample (2 mL/10 mL) of 1 and 2-naphthol by HLA/GO

1-Naphthol			2-Naphthol		
Actual (µg/mL)	Found-(µg/mL) ±SD[a]	Recovery (%)	Actual (µg/mL)	Found(µg/mL) ±SD[a]	Recovery (%)
1.50	1.56±0.01	104.00	4.50	4.37±0.06	97.11
2.00	2.00±0.04	100.00	2.00	2.01±0.01	100.50
2.00	2.06±0.04	103.00	8.00	8.14±0.01	101.75
7.50	7.38±0.02	98.40	5.50	5.61±0.02	102.00
6.00	6.05±0.01	100.83	12.00	12.05±0.01	100.41
7.00	6.87±0.06	98.14	3.00	3.09±0.01	103.00

[a]Standard deviation

Figures of merit

The selectivity (SEL), sensitivity (SEN), limit of detection (LOD), and analytical sensitivity (γ) can be calculated with HLA/GO method and used for the proposed method performance. The SEL is a measure of the degree of overlap and it shows the part of the total signal which is not lost due to spectral overlap. The selectivity in multivariate calibration can be defined by resorting to NAS calculations.

$$SEL = \frac{\left\|S^*\right\|}{\left\|S^*\right\|} \quad (7)$$

On the other hand, the SEN shows to what extent the response due to a particular analyte varies as a function of its concentration.

$$SEN = \left\|S^*\right\| \quad (8)$$

Where ‖S*‖ is the pure spectrum norm of the *i* analyte of interest and ‖S‖ is the total spectrum norm of the test samples. Also, analytical sensitivity can be expressed as:

$$\gamma = \frac{SEN}{\left\|S^*\right\|} \quad (9)$$

And the following equation has been proposed for estimating the LOD:

$$LOD = 3\|\varepsilon\|.\|S\| \quad (10)$$

Where ‖ε‖ is a measure of the instrumental noise. The value of ‖ε‖ may be estimated, in turn, by registering the spectra for several blank samples, calculating the norm of the NAS for each sample, and the corresponding standard deviation [24]. Table 4, presents the figures of merit SEL, SEN, Υ^{-1}, LOD, and statistical parameters, PRESS, REP, RMSEP, RSEP, R^2.

Table 4. Prediction statistical parameters obtained by application of HLA/GO analysis

Statistical	1-naphthol	2-naphthol
Spectral range (nm)	250-340	250-340
PRESS [a]	0.30	0.29
REP (%)	0.44	0.25
RMSEP	0.082	0.10
RSEP	1.65	1.48
R^2	0.9984	0.9996
SEL	0.39	0.28
SEN	2.03	1.37
Υ^{-1} (µg/mL)	0.14	0.13
LOD (µg/mL)	0.04	0.06

[a]Calculated using 2 factors

Comparison of the proposed method with other methods

A comparison of the analytical parameters of the HLA method with some of the previously proposed methods of the analytes is presented in Table 4. Also, the analysis time for this method was shorter than other methods particularly chromatographic methods. The repeatability of the methods was investigated using three repeat measurements of a 4 (µg/mL) 1, 2-naphthol was 3.60 and 2.30 % for 1, 2-naphthol respectively. The proposed method rates best in comparison with other approaches because it is simple, cheap, powerful; produces better results, non-polluting; possesses much simpler calibration models, highly sensitive and repeatable.

Table 5. Comparison of analytical parameters of the proposed method with some of the methods reported in literature

Method	Analyte	Instrument	LR	LOD	RSD (%)	Recovery (%)	Refs.
Direct	1-naphthol	HPLC[a]	15 – 120 (µg/L)	1.50 (µg/L)	2.00 – 7.20	100 - 120	32
	2-naphthol		15 – 120 (µg/L)	0.50 (µg/L)	2.40 – 5.40	89 - 95	
Direct	1-naphthol	Spectrofluorimeter	10 – 100 (µg/L)	-	-	80 - 120	9
	2-naphthol		5 – 20 (µg/L)	-	-	70 - 110	
CPE[b]	1-naphthol	Capillary Electrophoresis	0.10- 5 (µg/L)	0.24 (µg/L)	5.66	101.3 - 103	8
	2-naphthol		0.10- 5 (µg/L)	0.20 (µg/L)	5.66	92.43- 100.70	
Direct	1-naphthol	DPV[c]	1×10^{-6} - 1×10^{-8} M	1.0×10^{-9} M	3.9	99- 100.02	11

Direct	2-naphthol	Spectrophotometer	1×10^{-6} - 1×10^{-8} M	1.0×10^{-9} M	-	99-100.70	Proposed method
	1-naphthol		1–8 (µg/mL)	0.04 (µg/mL)	3.61	98-104	
	2-naphthol		1–16 (µg/mL)	0.06 (µg/mL)	2.3	97-103	

Conclusion

The use of the correction of a HLA allowed the simultaneous determination of a mixture of 1 and 2-naphthol in wastewater samples containing unknown interferences. The least EI, calculated using the NASRP, allowed the selection of the favorable wavelength range for the determination. The choice of the wavelength range is important in this specific application because of the high absorption signal and the nature is highly variable from the wastewater sample. Without previous sample preparation steps, wastewater samples were performed. The analytical figures of merit can be calculated by this method.

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