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Short communication

Spectrophotometric simultaneous determination of nitrophenol isomers by orthogonal signal correction and partial least squares

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Abstract

A simple, novel and sensitive spectrophotometric method was described for simultaneous determination of nitrophenol isomers mixtures. All factors affecting on the sensitivity were optimized and the linear dynamic range for determination of nitrophenol isomers were found. The simultaneous determination of nitrophenol mixtures by using spectrophotometric methods is a difficult problem, due to the spectral interferences. The partial least squares modeling was used for the multivariate calibration of the spectrophotometric data. The orthogonal signal correction was used for preprocessing of data matrices and the prediction results of model, with and without using orthogonal signal correction, were statistically compared. The experimental calibration matrix was designed by measuring the absorbance over the range 300–520 nm for 21 samples of 1–20, 1–20 and 1–10 μg ml^{-1} of *m*-nitrophenol, *o*-nitrophenol and *p*-nitrophenol, respectively. The RMSEP for *m*-nitrophenol, *o*-nitrophenol and *p*-nitrophenol with and without OSC were 0.3682, 0.5965, 0.3408 and 0.7351, 0.9962, 1.0055, respectively. The proposed method was successfully applied for the determination of *m*-nitrophenol, *o*-nitrophenol and *p*-nitrophenol in synthetic and real matrix samples such as water.

Keywords: Nitrophenol isomers; Spectrophotometric; Determination; Partial least squares; Orthogonal signal correction

1. Introduction

Nitrophenols belong to major phenolic pollutants that have been analysed in the environment. Nitrophenols, coming from pesticide degradation products, car exhaust, and industrial waters are listed as priority pollutions by the US Environmental Protection Agency [1,2]. They have great potential toxicities of carcinogenesis, teratogenesis, and mutagenesis [3]. Because of their detriment and vast scale distribution in the ecological environment, their separation and determination have been become one of the important studies of environmental analysis.

A number of analytical methods have been described in the literature for the determination of nitrophenols, including spectrophotometry [4–8], fluorescence [9], gas chromatography (GC) [10], high performance liquid chromatography (HPLC) [11,12] and capillary electrophoresis [3,13]. Traditional spectrophotometry and colorimetric methods are easily interfered by related compounds. GC methods can sometimes require relatively expensive reagents and need beneficiation and derivatization before analysis and it cannot be used directly to aqueous samples. HPLC and capillary electrophoresis methods are good alternative methods, but it need high cost to buy columns and waste more organic solvents.

In this paper, we report the investigation and development of rapid analytical methodology for the simultaneous prediction of three nitrophenols. The method is based on UV spectrophotometry, and the resulting heavily overlapping responses are processed by chemometrics. The application of chemometrics allows the interpretation of multivariate and is vital to the success of the simultaneous determination of the organic components. Conversely, the continuing research, development and verification of such novel methods as described here, continues to emphasize the significant potential of chemometrics in practical, modern chemical and multicomponent analysis. The advantage of multicomponent analysis using multivariate calibration is the speed in the determination of components in a mixture, avoiding preliminary separation step.

The application of quantitative chemometrics methods, particularly partial least squares (PLS) to multivariate chemical data is becoming more widespread owing to the availability

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of digitized spectroscopic data and commercial software for laboratory computers [14]. Other advantages of robust multivariate methods such as PLS are that they can be performed by ignoring the concentration of all other components except the analyte of interest. Each method needs a calibration step where the relationship between the spectra and the component concentration is deduced from a set of reference samples, followed by a prediction step in which the results of the calibration are used to determine the component concentrations from the sample spectrum. The basic concept of PLS was originally described by Wold [15,16] and consequently different algorithms for PLS modeling were developed [17–22]. In addition, several multicomponent determinations based on the application of these methods to spectrophotometric data have been reported [23–28]. Preprocessing methods can be applied in such situations to enhance the relevant information to make resulting models simpler and easier to interpret. Wold et al. [29] introduced orthogonal signal correction (OSC) as a preprocessing step that improves the calibration model by filtering strong structured variation in X that not correlated to Y. Since then, several groups [30–35] have been presented various OSC algorithms in the literature. Recently, application of orthogonal signal correction in UV–vis spectrophotometry simultaneous determination by partial least squares reported [36,37].

The aim of this paper was to investigate, for the first time, the possibility of using direct spectrophotometry and PLS methods for quantifying nitrophenols, such as *m*-nitrophenol, *o*-nitrophenol and *p*-nitrophenol, in synthetic and real matrix samples such as different water samples. The results obtained, with and without using OSC algorithm as a preprocessing treatment of original data, were compared. The aim of this work is to propose orthogonal signal correction and partial least squares (OSC–PLS) method to resolve ternary mixtures of nitrophenol isomers in synthetic and spike samples without prior separation. To our knowledge this is the first spectrophotometric report on the direct determination of nitrophenol, without any primary chemical reaction or separating steps.

2. Experimental

2.1. Chemicals

All the chemicals used were of analytical reagent grade, subboiling, distilled water was used throughout. Stock solutions of nitrophenol isomers were purchased from Fluka. Acetic acid, phosphoric acid, boric acid and sodium hydroxide were purchased from Merck. Standards of working solution were made by appropriate dilution daily as required. Adjusting the pH values of the working solutions was carried out using universal buffers (acetic acid–phosphoric acid–boric acid mixture) for this study [38].

2.2. Instrumentation and software

A Perkin Elmer (Lambda 25) spectrophotometer controlled by a computer and equipped with a 1-cm path length quartz cell was used for UV–vis spectra acquisition. Spectra were acquired between 300 and 520 nm (1 nm resolution). A HORIBA M-12 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 data were treated in an AMD 2000 XP (256 Mb RAM) microcomputer using MATLAB software, version 6.5 (The MathWorks). OSC and PLS calculus were carried out in the 'PLS Toolbox', version 2.0 (Eigenvector Technologies).

Table 1
Concentration data of the different mixtures used in the calibration set for the determination of nitrophenol isomers ($\mu g\,ml^{-1}$)

Mixture	*Meta*	*Ortho*	*Para*
M1	1.0	1.0	10.0
M2	4.8	1.0	8.2
M3	8.6	1.0	6.4
M4	12.4	1.0	4.6
M5	16.2	1.0	2.8
M6	20.0	1.0	1.0
M7	16.2	4.8	1.0
M8	12.4	8.6	1.0
M9	8.6	12.4	1.0
M10	4.8	16.2	1.0
M11	1.0	20.0	1.0
M12	1.0	16.2	2.8
M13	1.0	12.4	4.6
M14	1.0	8.6	6.4
M15	1.0	4.8	8.2
M16	4.8	4.8	6.4
M17	8.6	4.8	4.6
M18	12.4	4.8	2.8
M19	4.8	8.6	4.6
M20	8.6	8.6	2.8
M21	4.8	12.4	2.8

2.3. Procedure

2.3.1. Standard calibration set

A mixture design was used to maximize statistically the information content in the spectra [39]. A training set of 21 samples was taken (Table 1). The concentrations of *m*-nitrophenol, *o*-nitrophenol and *p*-nitrophenol were between 1.0–20.0, 1.0–20.0 and 1.0–10.0 $\mu g\,ml^{-1}$ varied, respectively. The mixed standard solutions were placed in a 10-ml volumetric flask and completed to the final volume with deionized water (final pH 9.0). The absorption spectra were recorded between 300 and 520 nm with scan rate of 600 nm min^{-1} against a blank of universal buffer.

2.3.2. Prediction set and analysis of real samples

For prediction set, 10 mixtures prepared that these not included in the previous set were employed as an independent test (Table 2). The real samples in this study were collected in waters from tap, river and waste (Table 4). The particulates of collected water were first removed by filter paper. The range of concentrations of *m*-nitrophenol, *o*-nitrophenol and *p*-nitrophenol were added to be 1.0–20.0, 1.0–20.0 and 1.0–10.0 $\mu g\,ml^{-1}$, respectively.

Table 2
Added and found results of synthetic mixtures of nitrophenol isomers by PLS and OSC–PLS methods ($\mu g\,ml^{-1}$)

Added			Found (PLS)			Recovery (%)			Found (OSC–PLS)			Recovery (%)		
Meta	*Ortho*	*Para*	*Meta*	*Ortho*	*Para*	*Meta*	*Ortho*	*Para*	*Meta*	*Ortho*	*Para*	*Meta*	*Ortho*	*Para*
2.0	2.0	2.0	1.74	1.78	2.11	87.0	89.0	105.5	1.94	1.86	2.06	97.0	93.0	103.0
20.0	20.0	10.0	18.44	22.31	12.23	92.2	111.6	122.3	19.12	21.34	10.75	95.6	106.7	107.5
2.0	12.0	6.0	1.79	11.02	5.48	89.5	91.8	91.3	1.94	11.58	6.05	97.0	96.5	100.8
7.0	15.0	2.0	8.05	14.23	1.68	115.0	94.9	84.0	7.24	14.74	1.89	103.4	98.3	94.5
12.0	11.0	9.0	11.41	9.86	10.51	95.1	89.6	116.8	11.69	10.21	9.48	97.4	92.8	105.3
2.0	2.0	8.0	1.67	1.76	8.79	83.5	88.0	109.9	1.93	1.88	8.22	96.5	94.0	102.8
18.0	18.0	8.0	17.36	18.12	7.59	96.4	100.7	94.9	17.56	18.02	7.68	97.6	100.1	96.0
8.5	8.5	6.0	8.97	7.68	5.38	105.5	90.4	89.7	8.55	7.85	6.13	100.6	92.4	102.2
17.0	8.0	8.0	16.21	7.45	9.05	95.4	93.1	113.1	16.56	7.77	8.41	97.4	97.1	105.1
2.0	15.0	8.0	1.79	14.20	8.44	89.5	94.7	105.5	1.84	14.38	8.12	92.0	95.9	101.5

3. Results and discussion

3.1. Spectrophotometric measurements

Fig. 1 shows the absorption spectra in aqueous solution of the individual nitrophenol isomers at pH 9.0. As this figure shows, there is a clear overlapping of the three spectra. This prevents the simultaneous determination of the nitrophenol isomers by direct UV–vis absorbance measurements. To overcome this problem a suitable and simple technique, which presents a good recovery, is PLS regression. Spectra of mixture of nitrophenol isomers solutions between 300 and 520 nm wavelengths by 1-nm intervals were recorded, and then the data were digitized and stored for late treatment.

3.2. Optimization of experimental condition

For the finding the optimum conditions, the influence of pH values on the spectrum of each nitrophenol isomers at a constant concentration of each isomers was studied. The formed isomers were affected differently with pH. In order to select the optimum pH value at which the minimum overlap occurs, influences of the pH of the medium on the absorption spectra of nitrophenol isomers were studied over the pH range 3.0–11.0. Fig. 2 shows the absorption spectra of nitrophenol isomers at various pH values. As it is observed in Fig. 2, at pH ranges 8.4–11.0, absorbance is almost unchanged. However pH 9.0 was chosen as the optimum pH for this work because both nitrophenol isomers have maximum absorbance and minimum overlap at this pH.

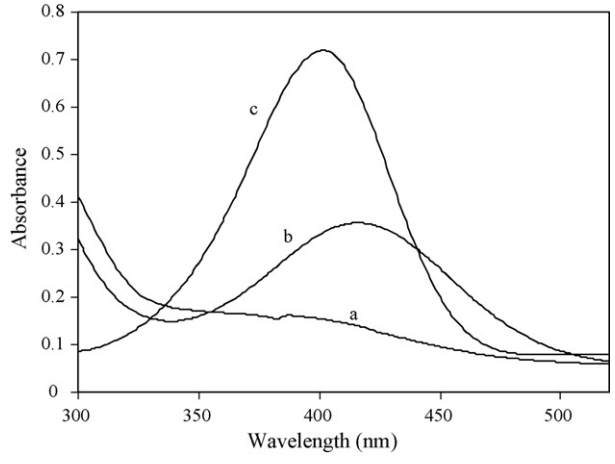

Fig. 1. Absorption spectra of the nitrophenol isomers at pH 9.0 and recorded against a blank of universal buffer: (a) $10\,\mu g\,ml^{-1}$ of *m*-nitrophenol, (b) $10\,\mu g\,ml^{-1}$ of *o*-nitrophenol and (c) $5\,\mu g\,ml^{-1}$ of *p*-nitrophenol.

Individual calibration curves were constructed with several points as absorbance versus nitrophenol isomers concentration. For constructing the individual calibration lines the absorbencies were measured at 380, 414 and 402 nm against a blank for *m*-nitrophenol, *o*-nitrophenol and *p*-nitrophenol, respectively. The linear regression equation for the calibration graph for *m*-nitrophenol for the concentration range of 1.0–20.0 $\mu g\,ml^{-1}$ was $A = 0.0305 + 0.0127C_{meta}$ ($r^2 = 0.9977$, $n = 13$), for *o*-nitrophenol for the concentration range of 1.0–20.0 $\mu g\,ml^{-1}$ was $A = 0.0409 + 0.0301C_{ortho}$ ($r^2 = 0.9949$, $n = 12$) and for *p*-nitrophenol for the concentration range of 1.0–10.0 $\mu g\,ml^{-1}$ was $A = 0.0107 + 0.1375C_{para}$ ($r^2 = 0.9989, n = 12$). The limits of detection were 0.44, 0.41 and 0.32 $\mu g\,ml^{-1}$ for *m*-nitrophenol, *o*-nitrophenol and *p*-nitrophenol, respectively, were calculated according to calibration lines characteristics.

3.3. Calibration and validation

A mixture design was used to maximize statistically the information content in the spectra. A training set of 21 samples was taken. The concentrations of *o*-nitrophenol, *m*-nitrophenol and *p*-nitrophenol were between 1.0–20.0, 1.0–20.0 and 1.0–10.0 $\mu g\,ml^{-1}$ varied, respectively. In Table 1 the compositions of the ternary mixtures used in the calibration matrices are summarized, and a diagrammatic representation of the mixture design is shown in Fig. 3. For prediction set, 10 mixtures prepared that these not included in the previous set were employed as an independent test (see Table 2). To ensure that the prediction and real samples are in the subspace of training set, the score plot of first principal component vs. second was sketched and all the samples are spanned with the training set scores.

The spectral region between 300 and 520 nm, which implies working with 220 experimental points per spectra (as the spectra are digitized each 1.0 nm), was selected for analysis, because this

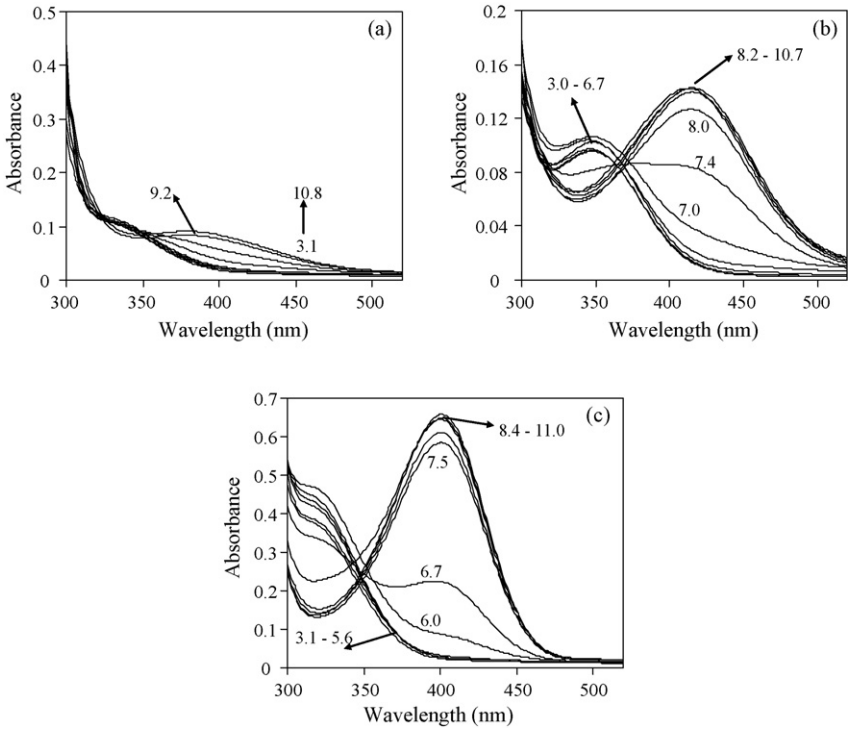

Fig. 2. Absorption spectra of (a) *m*-nitrophenol (4.3 μg ml^{-1}), (b) *o*-nitrophenol (3.4 μg ml^{-1}) and *p*-nitrophenol (4.6 μg ml^{-1}) at different pH.

is the zone with the maximum spectral information from the mixture components of interest. All absorption data are pretreated by mean-centering and scaling.

3.4. Preprocessing by orthogonal signal correction

Orthogonal signal correction (OSC) is a preprocessing technique used for removes the information unrelated to the target variables based on constrained principal component analysis. OSC is a suitable preprocessing method for partial least squares calibration of mixtures without loss of prediction capacity using spectrophotometric method. For calibration set three OSC components were used for filtering. Evaluation of the prediction errors for the validation set reveals that the OSC treated data give substantially lower root mean squares error of prediction values than original data. Also, the OSC-filtered data give much simpler calibration models with fewer components than the ones based on original data (Table 3). The results imply that the OSC method indeed removes information from UV–vis data that is not necessary for fitting of the *Y*-variables. In some cases the OSC method also removes non-linear relationships between *X* and *Y*. Fig. 3 shows the score plot for when the PLS and OSC–PLS are used. The score plots are shown for comparison of the results obtained from PLS and OSC–PLS. The results show, score plots have better results when OSC–PLS is used. Score plots reveal the geometrical placement of the solutions in principal components space. The experimental noise can destroy this relation but by removing the noise using OSC filtering, the OSC–PLS score plot (Fig. 3b) depict in a more clear way.

Table 3
Statistical parameters of the optimized matrix using the OSC–PLS and PLS

Nitrophenol isomers	NPC[a]	PRESS	RMSEP	RSEP (%)
m-Nitrophenol[b]	5	0.5385	0.7351	6.4614
o-Nitrophenol[b]	4	0.4725	0.9962	7.9173
p-Nitrophenol[b]	4	0.2643	1.0055	13.9844
m-Nitrophenol[c]	4	0.0748	0.3682	3.2362
o-Nitrophenol[c]	4	0.0545	0.5965	4.7401
p-Nitrophenol[c]	3	0.0708	0.3408	4.7393

[a] Number of principal component.
[b] Using PLS.
[c] Using OSC–PLS.

3.5. Selection of the optimum number of factors

The optimum number of factors (latent variables) to be included in the calibration model was determined by computing the prediction error sum of squares (PRESS) for cross-validated models using a high number of factors (half the number of total standard + 1), which is defined as follows:

$$\text{PRESS} = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2$$

where y_i is the reference concentration for the *i*th sample and $\hat{y}_i$ represents the estimated concentration. The cross-validation method employed was to eliminate only one sample at a time and then PLS calibrate the remaining standard spectra. By using this calibration the concentration of the sample, left out was predicted. This process was repeated until each standard had been left out once.

One reasonable choice for the optimum number of factors would be that number which yielded the minimum PRESS. Since

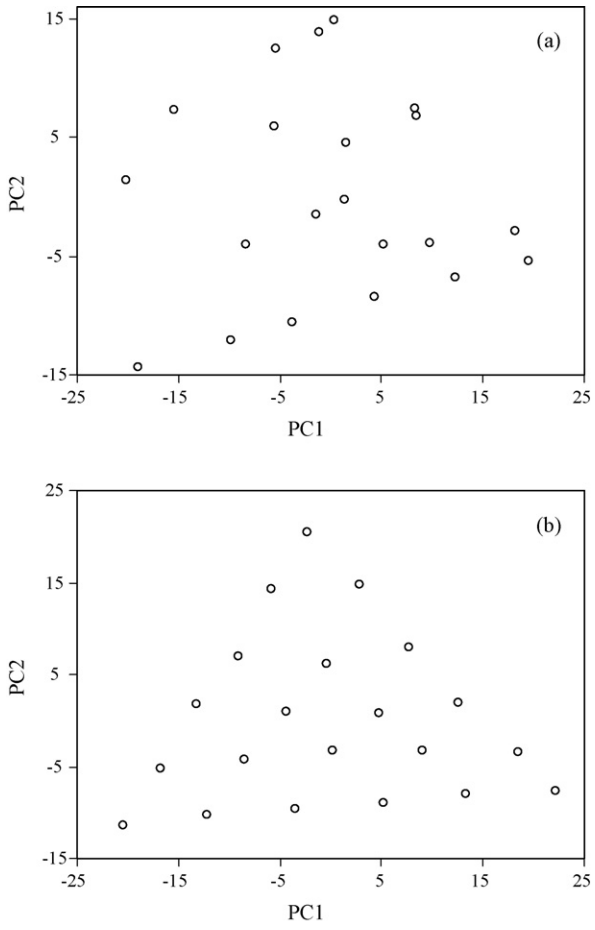

Fig. 3. Plots of first principal component against second principal component for nitrophenol isomers determination (a) by PLS model and (b) by OSC–PLS model.

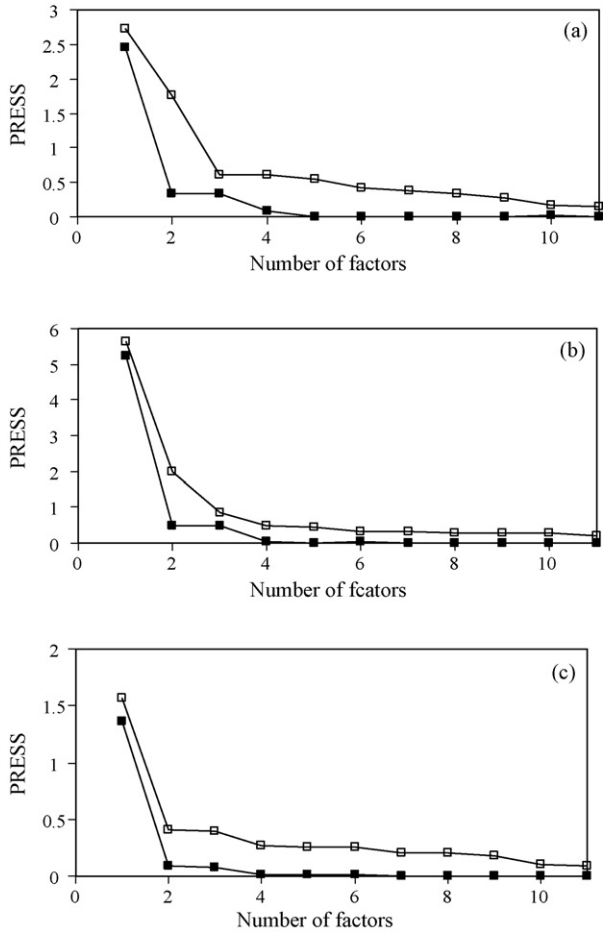

Fig. 4. Plots of PRESS versus number of factors by PLS (□) and OSC–PLS (■). (a) *m*-Nitrophenol, (b) *o*-nitrophenol and (c) *p*-nitrophenol.

there are a finite number of samples in the training set, in many cases the minimum PRESS value causes overfitting for unknown samples that were not included in the model. A solution to this problem has been suggested by Haaland et al. [40,41] in which the PRESS values for all previous factors are compared to the PRESS value at the minimum. The *F*-statistical test can be used to determine the significance of PRESS values greater than the minimum. The maximum number of factors used to calculate the optimum PRESS was selected as 11 and the optimum number of factors obtained by the application of PLS and OSC–PLS models are summarized in Table 3. In all instances, the number of factors for the first PRESS values whose F-ratio probability drops below 0.75 was selected as the optimum. In Fig. 4, the PRESS obtained by optimizing the calibration matrix of the absorbance data with PLS and OSC–PLS models is shown.

3.6. Determination of nitrophenol isomers in synthetic mixtures

The predictive ability of method was determined using 10 three-component nitrophenol isomers mixtures (their compositions are given in Table 2). The results obtained by applying PLS and OSC–PLS algorithm to seven synthetic samples are listed in Table 2. Table 2 also shows the recovery for prediction series of nitrophenol isomers mixtures. As can be seen, the recovery was also quite acceptable.

3.7. Statistical parameters

For the evaluation of the predictive ability of a multivariate calibration model, the root mean square error of prediction (RMSEP) and relative standard error of prediction (RSEP) can be used [42]:

$$\mathrm{RMSEP} = \sqrt{\frac{\sum_{i=1}^{n}(y_{\mathrm{pred}} - y_{\mathrm{obs}})^2}{n}},$$

$$\mathrm{RSEP}\ (\%) = \sqrt{\frac{\sum_{i=1}^{n}(y_{\mathrm{pred}} - y_{\mathrm{obs}})^2}{\sum (y_{\mathrm{obs}})^2}} \times 100$$

where y_{pred} is the predicted concentration in the sample, y_{obs} is the observed value of the concentration in the sample and n is the number of samples in the validation set. The value of RMSEP and RSEP (%) for nitrophenol isomers summarized in Table 3.

Table 4
OSC–PLS results applied on the real matrix samples ($\mu g\,ml^{-1}$)

Type of water[a]	*m*-Nitrophenol				*o*-Nitrophenol				*p*-Nitrophenol			
	Added	Found[b]	S.D.[c]	Recovery (%)	Added	Found[b]	S.D.[c]	Recovery (%)	Added	Found[b]	S.D.[c]	Recovery (%)
River	4.0	3.56	3.16	89.0	8.0	7.34	2.13	91.8	6.0	6.44	2.56	107.3
Waste	8.0	7.09	2.89	88.6	10.0	10.16	1.56	101.6	4.0	3.57	3.12	89.3
Waste	6.0	5.14	3.05	85.7	6.0	5.48	3.43	91.3	2.0	1.86	4.02	93.0
Tap	10.0	9.78	2.33	97.8	4.0	3.77	3.75	94.3	8.0	7.45	2.63	93.1

[a] All water samples are collected from Arak city.
[b] Mean of three measurements.
[c] Relative standard deviation for $n = 3$.

3.8. Application

The accuracy and precision of the proposed method as applied to the determination of the nitrophenol isomers in the real matrix samples were checked via a recovery study. To this end, aliquots of solutions of the nitrophenol isomers were supplied with variable amounts, between 1.0–20.0, 1.0–20.0 and 1.0–10.0 $\mu g\,ml^{-1}$ for *m*-nitrophenol, *o*-nitrophenol and *p*-nitrophenol, respectively, and their absorbance recorded. As can be seen from Table 4, the results obtained in the determination of nitrophenol isomers in water samples (river, waste and tap water) were quit good. In fact, the recoveries ranged from 85.7 to 97.8% for *m*-nitrophenol, 91.3 to 101.6% for *o*-nitrophenol and 89.3 to 107.3% for *p*-nitrophenol. Therefore, the OSC–PLS model is able to predict the concentrations of each nitrophenol isomers in the real matrix samples.

4. Conclusion

The *m*-nitrophenol, *o*-nitrophenol and *p*-nitrophenol mixture is an extremely difficult complex system due to the high spectral overlapping observed between the absorption for these nitrophenol isomers. In order overcome drawback, PLS and OSC–PLS multivariate calibration approaches were applied and compared. Analysis of the results for ternary mixtures showed that the use of PLS leads to significantly less-accurate prediction. The predicted values are obtained by application of OSC–PLS model for absorbance data show the high prediction ability of the OSC–PLS method. To our knowledge this is the first spectrophotometric report on the direct determination of nitrophenol isomers, without any primary chemical reaction or separating steps in synthetic and natural water samples.

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