Available online at www.sciencedirect.com
ScienceDirect
Microchemical Journal 85 (2007) 194–200
MICROCHEMICAL JOURNAL
www.elsevier.com/locate/microc

Successive projections algorithm improving the multivariate simultaneous direct spectrophotometric determination of five phenolic compounds in sea water

María S. Di Nezio [a], Marcelo F. Pistonesi [a], Wallace D. Fragoso [b], Márcio J.C. Pontes [b], Héctor C. Goicoechea [c], Mário C.U. Araujo [b], e Beatriz S. Fernández Band [a,*]

[a] *Lab. FIA, Departamento de Química, Universidad Nacional del Sur, Argentina*
[b] *Departamento de Química, Universidade Federal da Paraíba, Brazil*
[c] *Laboratorio de Desarrollo Analítico y Quimiometría (LADAQ), Cátedra de Química Analítica I, Facultad de Bioquímica y Ciencias Biológicas, Universidad del Litoral, Argentina*

Received 13 March 2006; received in revised form 28 April 2006; accepted 28 April 2006
Available online 14 June 2006

Abstract

This paper proposes an analytical method to determine directly and simultaneously five phenolic compounds (4-nitrophenol, 2-nitrophenol, phenol, 2,4,6-trichlorophenol and 4-chlorophenol) in sea water (Ria de Bahía Blanca, Argentine). The advantages of this method is that only requires spectrophotometric measurements (separation steps and derivatization reagents are avoided) and chemometric modelling (PLS and MLR–SPA).

The statistical comparison between PLS — a well established multivariate method — and MLR–SPA — a recently presented chemometric modelling — demonstrated better analytical performance for the later one. This fact is indicative of the potentiality of MLR–SPA for solving complex analytical problems.

Keywords: Phenol; Environmental; Wastes; PLS; SPA

1. Introduction

Phenol and substituted phenols are of special concern owing to the potential propagation of these compounds through the environment via leaching which comes from the industrial and petrochemical industries wastes. Some waterways can be contaminated for those phenols and hazard effects may occur to the people, also to aquatic organisms, fish and other life forms [1].

Furthermore, phenolic compounds are also formed during the natural decomposition of humic substances, tannins and lignins, and photolytic or metabolic degradation of herbicides and insecticides [2,3]. These compounds show toxicity values from moderate to higher, the toxicity level depends on the number, position and kind of substituent. The environmental aspects have became increasingly important in recent years and both the US Environmental Protection Agency (EPA) and the European Union (EU) have included the phenolic compounds as 4-nitrophenol, 2-nitrophenol, phenol, 2,4,6-trichlorophenol and 4-chlorophenol because they are considered dangerous pollutants [4,5]. The analysis established by EPA is based on liquid–liquid extraction (LLE), followed by gas chromatography (GC) using several detection methods (electron-capture detection (ECD) and mass spectrometry (MS) [6,7]. Thus, this method is complicated and it implies some disadvantages as time-consuming, high costs, also a large sample volume and toxic organic solvents are required to extract the analyte.

A more recent extraction technique, solid-phase microextraction (SPME), coupled to high-performance liquid chromatography (HPLC) with UV and electrochemical detection (ED) [8,9], or coupled to gas chromatography–mass spectrometry

---

* Corresponding author.
E-mail address: usband@criba.edu.ar (B.S. Fernández Band).

0026-265X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.microc.2006.04.021

[10,11] has been applied to the extraction of organic pollutants in environmental matrices, mainly in water samples, at trace levels.

Partial least-squares (PLS) is the most popular linear regression method that has been proposed for multicomponent analysis, and it is usually applied for multivariate calibration because of the quality of the calibration models and the availability of software [12,13]. PLS shows the advantage of using full data points, which is critical for the spectroscopic resolution of complex mixtures of analytes.

Nevertheless the PLS advantages, this method gives complex models owing to the fact that PLS employs latent variables instead of real variables, which may not have a straightforward physical interpretation. In this context, multivariate linear regression (MLR) models are simpler and easier to interpret, but they are very affected by collinearity between variables [13,14]. The use of the Successive Projections Algorithm (SPA) [15,16] like a variable selection strategy resolves this problem finding a small representative set of spectral variables with a minimum of collinearity. In terms of prediction ability, MLR–SPA has been shown to be comparable to full-spectrum PLS/PCR models in a number of applications, including UV–Vis [15,17], ICP-AES [15] and NIR [18]. Furthermore, SPA has also been compared with the genetic algorithm [15,16], which is a popular tool for variable selection in multivariate calibration [19,20]. Moreover, SPA is a deterministic algorithm, which does not employ stochastic operations such as other selection methods (Simulated Annealing [19] and Genetic Algorithm [21,22], for instance) do.

The final goal of the present study is to propose an analytical method to determine five phenols in a mixture without any separation step and without derivatization reagent. The method only requires the spectral data to be modelled by a multivariate calibration methods (PLS or MLR–SPA).

This method was applied to sea water samples, that were taken in the Ria of Bahía Blanca, Argentine. Whereas Bahía Blanca City has a Petrochemical pole, the town Council has included phenolic compounds in the lists of priority pollutants and periodical controls are being carried out. These compounds are included into the National Law 24051, decree–Law 831/93 about hazard residues. In effluents of the Petrochemical pole mixtures of different kinds and amounts of phenolic compounds have been found. As these mixtures had different composition and this composition is variable periodically. Thus, we selected five of the most probably phenol compounds that has been found in the controls.

2. Experimental

2.1. Apparatus

Spectrophotometric measurements were performed on a Hewlett Packard 8452A diode array spectrophotometer with a quartz cell with 10 mm light path.

Ultrasonic bath TESTLAB (tb04) was used.

Peristaltic pump Gilson Minipuls3.

2.2. Reagents and solutions

All solutions were prepared with analytical reagent-grade chemicals and ultra pure water of Milli-Q quality (18.3 mΩ). Stock solutions of 4-chlorophenol 0.0988 g L^{-1} (Fluka), phenol 0.102 g L^{-1} (Anedra), 2-nitrophenol 0.0988 g L^{-1} (Riedel de Häen), 4-nitrophenol 0.101 g L^{-1} (Merck) and 2,4,6-trichlorophenol 0.102 g L^{-1} (ICN Biomedicals) were prepared by weighing an appropriate amount and dissolving them in ultra pure water. They were mixed in an ultrasonic bath for 2 min. NH_4OH (Cicarelli) 0.01 mol L^{-1} was prepared dissolving 0.68 mL of the reagent and making up to 1000 mL with water. NH_4Cl–NH_4OH (pH 10.5) was prepared mixing an appropriate amount of NH_4Cl (Anedra) 2.0 mol L^{-1} and NH_4OH (Cicarelli) 2.0 mol L^{-1}. Na_2CO_3 (Fluka) 0.1 mol L^{-1} was prepared dissolving 8.3 g of the reagent and making up to 1000 mL with water. Britton–Robinson buffers were prepared mixing an appropriate amount of CH_3COOH (Cicarelli) 0.04 mol L^{-1}, H_3PO_4 (Merck) 0.04 mol L^{-1}, H_3BO_3 (Cicarelli) 0.04 mol L^{-1} and NaOH (Anedra) 0.2 mol L^{-1}.

2.3. Procedure

2.3.1. Matrix free of phenol compounds (MFPC) preparation

In this work standards were prepared by using a matrix free of phenol compounds (MFPC). The purpose of using this matrix is modelling the data by chemometric tools. That means the modelling of the matrix in order to prevent the interferences that can be present in the matrix.

The MFPC was prepared from a sea water sample, that was filtered through a glass microfibre (GF/C Whatman). The filtered sample was introduced into a FIA system by a peristaltic pump at 1.2 ml min^{-1}. This stream went through a mini-column packed with C18 (length: 150 mm and 4.6 mm i.d.). The C18 column was previously conditioned by pumping water for 1 min., then methanol for 2 min. and a final wash with water for 1 min.

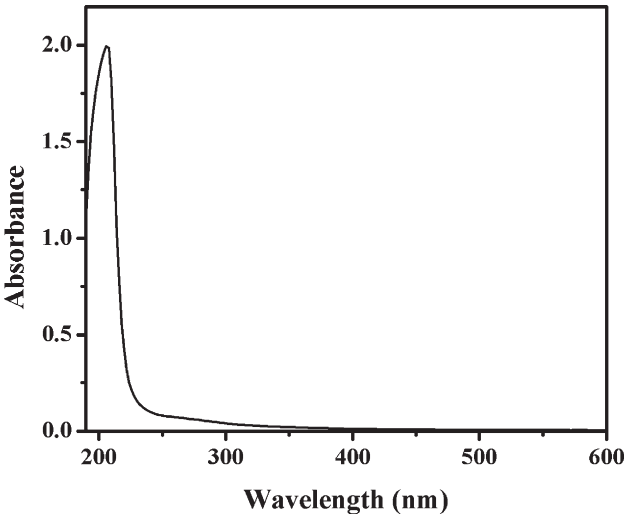

Fig. 1. The MFPC spectrum.

By this way the sample matrix totally free of organic compounds was obtained in order to use it for the calibration and validation mixtures preparation. Fig. 1 shows the spectra of the MFPC.

2.3.2. Calibration and validation sets

The calibration mixtures were prepared following a central composite design, which consisted of a combination of a fractional factorial design at two levels and an additional star design [23,24]. In this way, 26 calibration samples were prepared in the following analytes concentration ranges: 0.0 to 0.391 mg L^{-1} for phenol, 4-nitrophenol and 2-nitrophenol, and 0.0 to 0.400 mg L^{-1} for 2,4,6-trichlorophenol and 4-chlorophenol (see Table 1). On the other hand, a ten samples validation set was prepared in order to validate the chemometric models. The analytes concentrations were chosen in a randomized way, but spanning the concentration range of the calibration set (see Table 3). Both sets were prepared by placing suitable amounts of each phenolic compound, 1.0 mL NH_4Cl–NH_4OH pH 10.5 and completing to 25.00 mL with the MFPC solution. All mixtures were measured in random order.

2.3.3. Sample preparation

Sea water samples were collected into plastic Van-Dorn bottles and stored at 4 °C. They were filtered through a glass microfibre (GF/C Whatman). The clear filtrate was then stored at 4 °C to minimize analyte biodegradation. Before the analysis, they were equilibrated to room temperature.

3. Results and discussion

3.1. Influence of pH in phenol compounds spectra

Fig. 2 shows the UV–Vis absorption spectra of 4-chlorophenol, phenol, 2-nitrophenol, 4-nitrophenol and 2,4,6-trichlorophenol at pH 10.5. As can be observed, there are strong overlapping of spectra. The variation of the phenolic compounds spectra were studied using different Britton–Robinson buffers in the pH range 2.2–13.1. The spectral behaviour showed that a better resolution and higher analyte absorbances were obtained at pH 10.5.

Different solutions at the pH selected and also, buffer solution at this very pH were tested (Na_2CO_3 0.1 mol L^{-1}, NH_4OH 0.01 mol L^{-1}, NH_4Cl–NH_4OH, Britton–Robinson). The best signals were obtained with NH_4Cl–NH_4OH.

3.2. Analytical performance

3.2.1. Application of PLS

This method involves a calibration step in which the relation between spectra and component concentrations is estimated from a set of reference samples, and a prediction step in which the results of the calibration are used to estimate the component concentrations in an unknown sample spectrum [13]. Herein, we implemented the PLS-1

Table 1
Calibration design for chemometric modelling

Calibration sample	4-chlrophenol (mg L^{-1})	Phenol	2-nitrophenol	4-nitrophenol	2,4,6-trichlorophenol
1	0.264	0.258	0.258	0.258	0.400
2	0.400	0.258	0.258	0.258	0.264
3	0.264	0.391	0.258	0.258	0.264
4	0.400	0.391	0.258	0.258	0.400
5	0.264	0.258	0.391	0.258	0.264
6	0.400	0.258	0.391	0.258	0.400
7	0.264	0.391	0.391	0.258	0.400
8	0.400	0.391	0.391	0.258	0.264
9	0.264	0.258	0.258	0.391	0.264
10	0.400	0.258	0.258	0.391	0.400
11	0.264	0.391	0.258	0.391	0.400
12	0.264	0.258	0.391	0.391	0.400
13	0.264	0.391	0.391	0.391	0.264
14	0.400	0.391	0.391	0.391	0.400
15	0	0.321	0.321	0.321	0.328
16	0.132	0.321	0.321	0.321	0.328
17	0.328	0	0.321	0.321	0.328
18	0.328	0.129	0.321	0.321	0.328
19	0.328	0.321	0	0.321	0.328
20	0.328	0.321	0.129	0.321	0.328
21	0.328	0.321	0.321	0	0.328
22	0.328	0.321	0.321	0.129	0.328
23	0.328	0.321	0.321	0.321	0
24	0.328	0.321	0.321	0.321	0.132
25	0.264	0.258	0.258	0.258	0.400
26	0.400	0.258	0.258	0.258	0.264

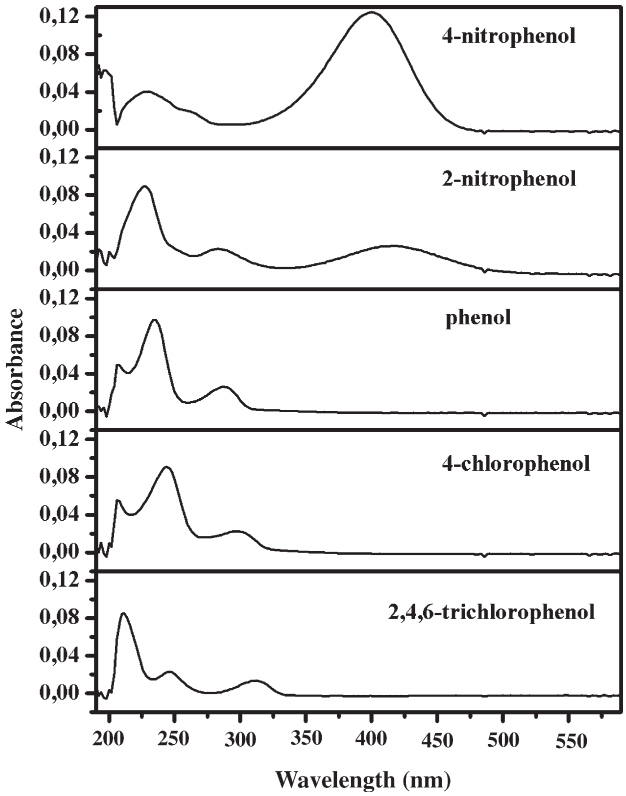

Fig. 2. UV–Vis spectra of the five phenol compounds, each one at a concentration of 0.1 mg L^{-1} and pH 10.5.

version that is optimised for the determination of a single analyte of interest (each of the five phenols in turn).

The optimum number of factors to be used within the PLS-1 algorithm is an important parameter to achieve better performance in prediction. This allows one to model the system with the optimum amount of information, avoiding overfitting. The well-known cross-validation procedure was applied in the present work. The optimum numbers of factors for different spectrum regions are shown in Table 2. Data region selection was performed by applying a moving window strategy to the calibration set itself, in order to find the most informative range in the time profile by localisation of the minimum prediction error sum of squares (PRESS) [25]. As can be seen, the obtained latent variables were higher than 5 in most of the cases, indicating that the variability sources number in the presently studied system exceeds the number of studied analytes.

Table 2 also gives other important statistical parameters and figures of merit such as the root mean square error of cross-validation (RMSECV), the relative error of prediction (REP %), the sensitivity (SEN_k), the selectivity (SEL_k), the analytical sensitivity (SEN_k) and the limit of detection (LOD_k). These latter figures of merit can be calculated and used for method comparison or to study the quality of a given analytical technique. SEN for a given analyte k has been defined as

$$\text{SEN}_k = \frac{1}{||\mathbf{b}_k||} \tag{1}$$

Where || || indicates the Euclidean norm and $\mathbf{b}_k$ is the vector of final regression coefficients appropriate for component k, which can be obtained by any multivariate method. Better insight is furnished by the analytical sensitivity, defined by

$$\gamma_k = (\text{SEN}_k/||\delta r||) \tag{2}$$

where $||\delta r||$ is a measure of the instrumental noise. It allows comparing analytical methods, regardless the specific technique equipment and scale employed. Moreover, it establishes the minimum concentration difference ($\gamma^{-1}{}_k$) which is statistically discernible by the method along the dynamic range [26].

The selectivity quantifies the amount of analyte signal that is overlapped with the interferences, and is calculated as

$$\text{SEL}_k = \frac{||\mathbf{s}_k^*||}{||\mathbf{s}_k||} \tag{3}$$

Where $\mathbf{s}_k$ is the vector of spectral sensitivities of component k in pure form and $\mathbf{s}_k^*$ is the corresponding projection onto the net analyte signal space [27].

Table 2
PLS calibration figures

Figures	4-chlrophenol (mg L^{-1})	Phenol	2-nitrophenol	4-nitrophenol	2,4,6-trichlorophenol
Spectral region (nm)	250–428	238–588	330–548	370–548	310–428
Optimal number of factors[a]	8	8	4	4	6
RMSECV[b] (mg L^{-1})	0.017	0.016	0.011	0.008	0.025
REP[c] (%)	5.8	5.3	3.8	2.7	8.3
SEN[d]d	0.027	0.048	0.067	0.19	0.013
SEL[d]	0.13	0.13	0.41	0.14	0.23
(γ^{-1})[d] (mg L^{-1})	0.037	0.021	0.015	0.0053	0.073
LOD[d] (mg L^{-1})	0.12	0.069	0.049	0.017	0.24

[a] Factors were selected following the Haaland criterion [12].

[b] $\text{RMSECV} = \sqrt{\frac{\Sigma(x_{\text{act}}-x_{\text{pred}})^2}{I}}$, where I is the number of calibration simples, x_{act} is the actual concentration in calibration samples, x_{pred} is the predicted concentration with the PLS models and $\overline{x}_{\text{act}}$ is the average concentration in the calibration set.

[c] $\text{REP}(\%) = \text{RMSECV} \times 100/\overline{x}_{\text{act}}$.

[d] Calculated according to Eqs. (1), (2), (3) and (4), respectively. $||\delta r||$ is a measure of the instrumental noise and equal to 0.001.

Table 3
PLS prediction on both validation and real samples

Validation samples	4-chlorophenol (mg L^{-1})		Phenol		2-nitrophenol		4-nitrophenol		2,4,6-trichlorophenol	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	0.239	0.217	0.245	0.240	0.239	0.232	0.243	0.253	0.388	0.409
2	0.379	0.349	0.245	0.284	0.239	0.232	0.243	0.252	0.245	0.259
3	0.379	0.358	0.388	0.375	0.239	0.233	0.243	0.250	0.388	0.407
4	0.319	0.297	0.326	0.344	0.159	0.145	0.324	0.333	0.326	0.353
5	0.159	0.126	0.326	0.354	0.000	−0.002	0.324	0.325	0.326	0.352
6	0.000	0.019	0.163	0.129	0.319	0.310	0.162	0.177	0.163	0.199
7	0.319	0.339	0.000	−0.006	0.379	0.351	0.385	0.390	0.163	0.177
8	0.239	0.238	0.388	0.325	0.379	0.385	0.000	0.021	0.388	0.426
9	0.319	0.310	0.326	0.352	0.319	0.301	0.385	0.391	0.000	−0.004
10	0.379	0.387	0.245	0.250	0.379	0.361	0.385	0.393	0.245	0.251
Real 1	0.159	0.142	0.286	0.256	0.319	0.310	0.203	0.217	0.326	0.358
Real 2	0.199	0.142	0.245	0.211	0.258	0.254	0.284	0.290	0.245	0.257
Real 3	0.358	0.393	0.245	0.233	0.279	0.291	0.243	0.246	0.368	0.376
Real 4	0.239	0.243	0.326	0.254	0.199	0.175	0.324	0.332	0.204	0.218
RMSEP [a](ppm)		0.025		0.034		0.014		0.010		0.022
REP%		9.6		12.6		5.2		3.7		8.2

[a] RMSEP $= \sqrt{\frac{\Sigma(x_{\text{act}}-x_{\text{pred}})^2}{I}}$, where I is the number of validation simples, x_{act} is the actual concentration in validation samples, x_{pred} is the predicted concentration with the PLS models and $\bar{x}_{\text{act}}$ is the average concentration in the validation n set.

At last, a usual definition for the limit of detection is [28]:

$$\text{LOD} = 3.3||\delta r|| \quad ||\mathbf{b}_k|| \tag{4}$$

LODs obtained show that the sensibility of the method agree well with the values previously reported for this type of sample [31–33] for phenol, 2-nithophenol and 4-nitrophenol (values ranged between 0.02 and 0.07 mg L^{-1}). On the other hand, LODs obtained for 4-chlorophenol and 2,4,6-trichlorophenol are not good enough for considering the methodology to the routine control.

Prediction results are shown in Table 3. As can be seen, relative error of prediction (REP%) values for the validation set samples are ranged from 3.7 (4-nitrophenol) to 12.6% (phenol). As will be seen bellow, these results are improved when using another chemometric tool.

3.2.2. Application of MLR–SPA

MLR–SPA uses a calibration (X_{cal}) and a validation (X_{val}) sets consisting of instrumental response data and parameter values measured by a reference method (y). The essence of SPA consists of projection operations carried out on the calibration matrix. A detailed explanation of the projection operations is given elsewhere [15,16].

Starting from each of the J variables (columns of X_{cal}) available for selection, SPA builds an ordered chain of K variables where each element is selected in order to present the least collinearity with the previous ones. The collinearity between variables is assessed by the correlation between the respective column vectors of X_{cal}. It is worth to point out that, according to this selection criterion, no more than K variables can be included in the chain [15,16].

It is possible to extract K subsets of variables from each of the J chains constructed by using one up to K elements in the order in which they were selected. Thus, a total of $J \times K$ subsets of variables can be formed. In order to choose the most appropriate subset, $J \times K$ MLR models are built using the calibration samples set and compared in terms of the root–mean–square error obtained of the validation samples set. Table 4 present the number of selected variables, these variables and figures of merit for SPA. The prediction results for SPA models are shown in Table 5.

Since it is not possible to assure that the selected variables by SPA are orthogonals, $||\mathbf{b}_k||$, SEN$_K$ and LOD$_K$ were not calculated for MLR–SPA.

Table 4
SPA calibration figures

Figures	4-chlorophenol	Phenol	2-nitrophenol	4-nitrophenol	2,4,6-trichlorophenol
Spectral region (nm)	250–428	238–588	330–548	370–548	310–428
Number of variable selected	17	11	10	6	6
Selected variables (nm)	250; 256; 264; 270; 282; 292; 304; 316; 340; 364–370; 378; 402; 426; 428	240; 250; 264; 288; 306; 340;402; 448; 486; 568; 586	330; 364–368; 400; 450; 486; 488; 498; 546.	370; 400; 428; 486; 488; 546.	310; 318; 332; 358; 402; 428.
RMSEC	0.005	0.007	0.008	0.005	0.014
REP (%)	1.7	2.2	2.6	1.6	4.4

Table 5
SPA prediction on both validation and real samples

Validation samples	4-chlorophenol (mg L^{-1})		Phenol		2-nitrophenol		4-nitrophenol		2,4,6-trichlorophenol	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	0.239	0.242	0.245	0.254	0.239	0.242	0.243	0.241	0.388	0.390
2	0.379	0.370	0.245	0.289	0.239	0.243	0.243	0.241	0.245	0.234
3	0.379	0.373	0.388	0.387	0.239	0.241	0.243	0.239	0.388	0.377
4	0.319	0.330	0.326	0.352	0.159	0.152	0.324	0.316	0.326	0.324
5	0.159	0.147	0.326	0.359	0.000	− 0.005	0.324	0.316	0.326	0.324
6	0.000	− 0.001	0.163	0.148	0.319	0.318	0.162	0.164	0.163	0.174
7	0.319	0.315	0.000	0.002	0.379	0.373	0.385	0.385	0.163	0.153
8	0.239	0.263	0.388	0.353	0.379	0.389	0.000	0.008	0.388	0.399
9	0.319	0.279	0.326	0.351	0.319	0.326	0.385	0.383	0.000	− 0.024
10	0.379	0.375	0.245	0.267	0.379	0.376	0.385	0.383	0.245	0.241
Real 1	0.159	0.160	0.286	0.276	0.319	0.320	0.203	0.210	0.326	0.328
Real 2	0.199	0.164	0.245	0.227	0.258	0.263	0.284	0.282	0.245	0.234
Real 3	0.358	0.368	0.245	0.251	0.279	0.288	0.243	0.248	0.368	0.350
Real 4	0.239	0.259	0.326	0.273	0.199	0.190	0.324	0.320	0.204	0.198
RMSEP (ppm)		0.018		0.026		0.006		0.005		0.011
REP%		6.6		9.8		2.2		1.8		4.1

3.2.3. Comparative study of both chemometric models

A visual inspection of Tables 3 and 5 allows seeing substantial differences between predictions obtained by application of both chemometric approaches. REP% values drop from 12.6% to 9.8% in the worst case (phenol) and from 5.2 to 2.2 for 2-nitrophenol. A statistical *t*-student test allowed us to conclude (not showed) that differences between REP% obtained for both approaches are significant ($p<0.05$) in all the five analytes.

In order to get further insight into the precision ability of both chemometric methods herein analysed, linear regression analysis of actual concentration values versus SPA and PLS predictions (see Tables 3 and 5) was applied. The estimated intercept and slope ($\hat{a}$ and $\hat{b}$ respectively) were compared with their ideal values of 0 and 1 using the elliptical joint confidence region (EJCR) test, in this case by using an ordinary least squares fitting (OLS) of the actual versus the simultaneously seventy predicted values for each method as recommended Martinez et al. for simultaneous determination of several analytes [29]. Fig. 3 shows the EJCR plots for the two employed chemometric assisted methods. As can be seen, the ellipses contain the theoretical ($a=0$, $b=1$) point for both methods. This fact is indicative that proportional and constant errors are not present and thereby of the excellent predictive ability especially of MLR–SPA.

3.2.4. Applications to real samples

The method was applied to sea water samples which were spiked with phenol compounds as they were found not to contain them initially. Bearing in mind the strong absorption of the matrix and phenol compounds at low wavelengths, the standards were prepared with the sea water free of phenol compounds. As can be judged observing the results presented in Tables 3 and 5, the prediction can be considered acceptable taking unto account the complexity of the sample being analyzed.

4. Conclusions

Five phenols that are considered dangerous pollutants could be directly and simultaneously determined in complex samples by resorting to spectrophotometric measurements and chemometric modelling. The statistical comparison between PLS — a well established multivariate method — and MLR–SPA — a recently presented chemometric modelling — has demonstrated a better analytical performance for the later one (i.e. a substantially diminishing on the error of prediction). This fact is indicative of the potentiality of MLR–SPA on solving complex analytical problems.

The method proposed in this paper, and applied to sea water, is a useful alternative for the determination of the phenolic compounds above mentioned, which are included in the EPA and European Union lists as hazardous pollutants. Moreover,

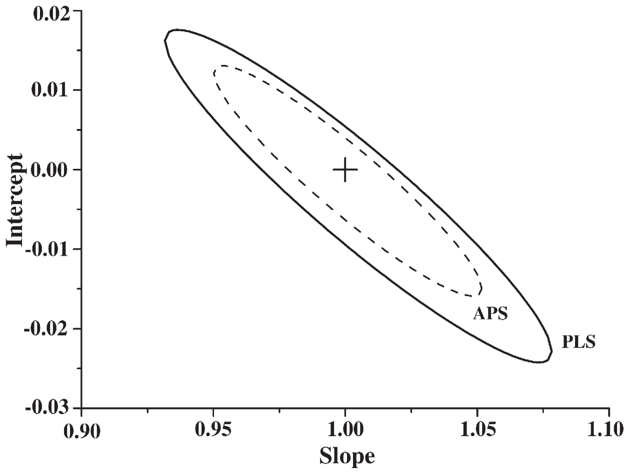

Fig. 3. Elliptical joint confidence regions for the slope (b) and intercept (a) corresponding to regressions of real concentrations versus PLS and MLR–SPA predicted concentrations of the five analytes. PLS (solid line) and MLR–SPA (dashed line). The cross marks the theoretical point ($a=0$, $b=1$).

the method presents several advantages such as good sensitivity and selectivity and an acceptable linear range compared with other methods [30,31].

Acknowledgements

The authors express their gratitude to the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) de la República Argentina. M.F. Pistonesi acknowledges the CIC (Comisión de Investigaciones Científicas de la Provincia de Buenos Aires). W. D. Fragoso acknowledges the Brazilian agencies: FAPESQ (Fundação de Apoio a Pesquisa do Estado da Paraíba) and CNPq (Conselho Nacional de Desenvolvimento e Científico e Tecnológioco) for the scholarship. This work was partially supported by the Universidad Nacional del Sur, Bahía Blanca, República Argentina.

References

[1] Y. Ni, L. Wang, S. Kokot, Simultaneous determination of nitrobenzene and nitro-substituted phenols by differential pulse voltammetry and chemometrics, Anal. Chim. Acta 431 (2001) 101–113.

[2] N. Masqué, E. Pocurull, R.M. Marcé, F. Borrull, Determination of eleven priority EPA phenolics at nanogram-per-litre levels by online solid-phase extraction and liquid chromatography with UV and electrochemical detection, Chromatographia 47 (1998) 176–182.

[3] A.S. Narang, Ch.A. Vernoy, G.A. Eadon, Evaluation of Nielsen–Kryger steam-distillation technique for recovery of phenols from soil, J. Assoc. Off. Anal. Chem. 66 (1983) 1330–1334.

[4] US EPA, Code of Federal Regulations, title 40, part 136, Washington DC, 1992.

[5] US EPA, SW-846, Office of Solid Wastes, Washington DC, 1997.

[6] EPA Method 604, Phenols in Federal register, Friday, Environmental Protection Agency Part VIII. CFR Part 136, vol. 40, 1984, pp. 58–66.

[7] EPA Method 8041, Phenols by Gas Chromatography: Capillary Column Technique, Washington, DC, 1995, pp. 1–28.

[8] A. Peñalver, E. Pocurull, F. Borrull, R.M. Marce, Solid-phase microextraction coupled to high-performance liquid chromatography to determine phenolic compounds in water samples, J. Chromatogr., A 953 (2002) 79–87.

[9] E. Gonzalez-Toledo, M.D. Prat, M.F. Alpendurada, Solid-phase microextraction coupled to liquid chromatography for the analysis of phenolic compounds in water, J. Chromatogr., A 923 (2001) 45–52.

[10] H. Bagheri, A. Saber, S.R. Mousavi, Immersed solvent microextraction of phenol and chlorophenols from water samples followed by gas chromatography–mass spectrometry, J. Chromatogr., A 1046 (2004) 27–33.

[11] M. Llompart, M. Lourido, P. Landýn, C. Garcýa-Jares, R. Cela, Optimization of a derivatization-solid-phase microextraction method for the analysis of thirty phenolic pollutants in water samples, J. Chromatogr., A 963 (2002) 137–148.

[12] E.V. Thomas, D.M. Haaland, Partial least-squares methods for spectral analyses. |I.| Relation to other quantitative calibration methods and the extraction of qualitative information, Anal. Chem. 60 (1988) 1193–1202.

[13] H. Martens, T. Naes, Multivariate Calibration, Wiley, London, 1993.

[14] T. Naes, B.H. Mevik, Understanding the collinearity problem in regression and discriminant analysis, J. Chemom. 15 (2001) 413–426.

[15] M.C.U. Araujo, T.C.B. Saldanha, R.K.H. Galvão, T. Yoneyama, H.C. Chame, V. Visani, The successive projections algorithm for variable selection in spectroscopic multicomponent analysis, Chemom. Intell. Lab. Syst. 57 (2000) 65–73.

[16] R.K.H. Galvão, M.F. Pimentel, M.C.U. Araujo, T. Yoneyama, V. Visani, Aspects of the successive projections algorithm for variable selection in multivariate calibration applied to plasma emission spectrometry, Anal. Chim. Acta 443 (2001) 107–115.

[17] H.A. Dantas Filho, E.S.O.N. Souza, V. Visani, S.R.R.C. Barros, T.C.B. Saldanha, M.C.U. Araújo, R.K.H. Galvão, Simultaneous spectrometric determination of Cu^{2+}, Mn^{2+} and Zn^{2+} in polivitaminic/polimineral drug using SPA and GA algorithms for variable selection, J. Braz. Chem. Soc. 16 (2005) 58–61.

[18] M.C. Breitkreitz, I.M. Raimundo Jr., J.J.R. Rohwedder, C. Pasquini, H.A. Dantas Filho, G.E. José, M.C.U. Araújo, Determination of total sulfur in diesel fuel employing NIR spectroscopy and multivariate calibration, Analyst 128 (2003) 1204–1207.

[19] C.B. Lucasius, M.L.M. Beckers, G. Kateman, Genetic algorithms in wavelength selection: a comparative study, Anal. Chim. Acta 286 (1994) 135–153.

[20] R. Leardi, Application of a genetic algorithm to feature selection under full validation conditions and to outlier detection, J. Chemom. 8 (1994) 65–79.

[21] D.J. Rimbaud, D.L. Massart, R. Leardi, O.E. de Noord, Genetic algorithms as a tool for wavelength selection in multivariate calibration, Anal. Chem. 67 (1995) 4295–4301.

[22] J.H. Kalivas, N. Roberts, J.M. Sutter, Global optimization by simulated annealing with wavelength selection for ultra-violet–visible spectrophotometry, Anal. Chem. 61 (1989) 2024–2030.

[23] H.C. Goicoechea, A.C. Olivieri, Sustained prediction ability of net analyte preprocessing methods using reduced calibration sets. Theoretical and experimental study involving the spectrophotometric determination of multicomponent mixtures, Analyst 126 (2001) 1105–1112.

[24] H.C. Goicoechea, A.C. Olivieri, Chemometric assisted simultaneous spectrophotometric determination of four-component nasal solutions with a reduced number of calibration samples, Anal. Chim. Acta 453 (2002) 289–300.

[25] M.S. Collado, V.E. Mantovani, H.C. Goicoechea, A.C. Olivieri, Simultaneous spectrophotometric-multivariate calibration determination of several components of ophthalmic solutions: phenylephrine, chloramphenicol, antipyrine, methylparaben and thimerosal, Talanta 52 (2000) 909–920.

[26] C.L. Rodríguez, A.M. García Campaña, C. Jiménez Linares, M. Román Ceba, Anal. Lett. 26 (1993) 1243–1258.

[27] H.C. Goicoechea, A.C. Olivieri, A comparison of orthogonal signal correction and net analyte preprocessing methods. Theoretical and experimental study, Chemom. Intell. Lab. Syst. 56 (2001) 73–81.

[28] A. Muñoz de la Peña, A. Espinosa Mansilla, D. Gonzalez Gomez, A.C. Olivieri, H.C. Goicoechea, Interference-free analysis using three-way fluorescence data and the parallel factor model. Determination of fluoroquinolone antibiotics in human serum, Anal. Chem. 75 (2003) 2640–2646.

[29] A. Martinez, J. Riu, O. Busto, J. Guasch, F.X. Rius, Validation of bias in multianalyte determination methods. Application to RP-HPLC derivatizing methodologies, Anal. Chim. Acta. 406 (2000) 257–278.

[30] Y. Ni, L. Wang, S. Kokot, Simultaneous determination of nitrobenzene and nitro-substituted phenols by differential pulse voltammetry and chemometrics, Anal. Chim. Acta 431 (2001) 101–113.

[31] A. Cladera, M. Miro, J.M. Estela, V. Cerdà, Multicomponent sequential injection analysis determination of nitro-phenols in waters by on-line liquid–liquid extraction and preconcentration Ana, Chim. Acta 421 (2000) 155–166.

[32] W. Zhang, N.D. Danielson, Determination of phenols by flow injection and liquid chromatography with on-line quinine-sensitized photo-oxidation and quenched luminol chemiluminescence detection, Anal. Chim. Acta 493 (2003) 167–177.

[33] K. Tsukagoshi, T. Kameda, M. Yamamoto, R. Nakajima, Separation and determination of phenolic compounds by capillary electrophoresis with chemiluminescence detection, J. Chromatogr., A 978 (2002) 213–220.