

Conductometric simultaneous determination of acetic acid, monochloroacetic acid and trichloroacetic acid using orthogonal signal correction-partial least squares

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Received 16 June 2005; received in revised form 30 August 2005; accepted 10 September 2005

Available online 19 October 2005

Abstract

A simultaneous conductometric titration method for determination of mixtures of acetic acid, monochloroacetic acid and trichloroacetic acid based on the multivariate calibration partial least squares is proposed. It is possible to obtain an adjustable model to relate squared concentration values of the mixtures used in the calibration range by conductance. The effect of orthogonal signal correction (OSC) as a preprocessing technique used to remove the information unrelated to the target variables is studied. The calibration model was build using conductometric titrations data of 16 mixtures of three acids. The concentration matrix was designed by a orthogonal design. The root mean squares error of prediction (RMSEP) for acetic acid, monochloroacetic acid and trichloroacetic acid with and without OSC were 0.08, 0.30 and 0.08, and 0.15, 0.40 and 0.18, respectively. The results obtained by OSC-PLS are better than the PLS and this indicate the successful application of the OSC filter as a good preprocessing method in multivariate calibration methods. The proposed procedure allows the simultaneous determination of these acids, in the synthetic mixtures. © 2005 Elsevier B.V. All rights reserved.

Keywords: OSC-PLS; Chloroacetic acid; Conductometric titration; Chemometrics

1. Introduction

Acetic acid (ethanoic acid) used to prepare dilute acetic acids and strong ammonium acetate solution, for destruction of warts, in eardrops, as an expectorant, liniment and astringent, in the manufacture of acetic anhydride, cellulose acetate, vinyl acetate, chloroacetic acid, plastics, pharmaceuticals, dyes, insecticides, laundry sour, photographic chemicals, vitamins, antibiotics, cosmetics and hormones. It is used as an antimicrobial agent, latex coagulant and oil-well acidifier, in textile printing, as a preservative in foods and as a solvent for gums, resins, volatile oils and many other substances [1].

Monochloroacetic acid is used in the manufacture of cellulose ethers (used mainly for drilling muds, detergents, food and pharmaceuticals), as a post-emergence contact herbicide and defoliant, and in the manufacture of glycine and thiogly-

colic acid. Chloroacetic acid is also used in the manufacture of various dyes, synthetic caffeine and organic chemicals [2].

Trichloroacetic acid used is highly soluble in water and, with a Henry's constant of $7.4 \times 10^4 \text{ mol kg}^{-1} \text{ atm}^{-1}$, the preferred environmental compartment where emissions will accumulate is the hydrosphere [3]. Three processes were used to manufacture trichloroacetic acid, exhaustive chlorination of acetic acid, oxidation of chloral (CCl_3CHO) using H_2O_2 and hydrolytic oxidation of perchloroethylene [4]. It has not been possible to estimate a global quantity of trichloroacetic acid manufactured but the estimated use in West Germany during the period "from the 1940s to 1990" was a total of about 30,000 t [5]. Apart from small quantities used as antiseptic, most of the manufactured material was used, in the form of sodium trichloroacetate, as herbicide [4]. Trichloroacetic acid is effective only in the control of monocotyledons, such as grasses. Potato, oil-seed rape, kale, turnip, spinach and flax are all highly resistant. Tomato, lettuce, alfalfa, clover, cotton, pea, sugar beet and bean plants may be grown after the ground has been treated with trichloroacetic acid [6]. So according to above paragraphs, which reflect an environ-

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mental impact of the acetic skeletal acids, there is a demand for a simple and a versatile method for the determination of mixtures of them.

In the titration of acid–base systems, the detection of endpoint usually depends on the use of visual indicators or potentiometric [7] and/or pH-metric [8] method. In binary or ternary mixtures of acids or bases if the differences between acidity constants of individual acids are less than four logarithmic units, it is impossible to have an accurate determination in these types of mixtures. Or in the case of the polyprotic acids if the differences between successive acidity constants are less than this critical value, i.e. the acids with overlapped acidity constants, we cannot observe all the titration endpoints and this problem prevents us from having a precise and quantitative determination from the volume of endpoints. Introducing of the multivariate statistical methods in the analytical chemistry create a suitable and easy to use device to tackle and remove such problems. As these methods use a whole data set in the course of titration (first order method) instead of a single or scalar datum (zero order methods such as endpoint in conventional titrations), gave good capability to these approaches to determine the concentrations of all constituents of a mixture. Nowadays almost in all industrial plants and clearly in all research analytical laboratories there are digital conductometric with computer controlled. Thus the conductometric titrations are performed automatically under full computer controlled.

Recently Ni [7,9] have used photometric titration data in a multivariate sense and determined the mixtures of different analytes simultaneously. In these cases what is important is that the measured variables must be transferred to a new space so that data can be represented as a general linear model, i.e. the observed conductance in the present case, can be related to the analyte concentration as:

$$\mathbf{Y} = \mathbf{B}\mathbf{X} + \mathbf{E}$$

where \mathbf{X} is the matrix of measured variables, \mathbf{Y} the concentration or a value which is explicitly related to concentrations of the sample constituents, \mathbf{B} contains the regression coefficients which relate measured variables to concentrations and \mathbf{E} is residual or measurement error matrix. The above equation can be used in any of soft modeling calibration models to model the conductometric variations in the course of a titration, with respect to some property such as initial concentrations of the sample constituents. It is known that the derivation of the above equation needs some mathematical steps [7] using chemical equilibrium relations. But fortunately in the soft modeling calibration methods, in spite of hard modeling like Gran's method [10], don't require to know such mathematical relationships and equilibrium constants. It is just necessary to keep in mind a linear model and after building the calibration model the pre-defined relation must be validated using some ways like residual variance analysis, inspection of residual plot to check the presence of any trend in residual values and physical meaning of the obtained properties in prediction step. Anyway we leave that derivation for the interested readers especially for computational or theoretical chemists.

Now a quantitative chemometrics method, particularly partial least squares (PLS) can be applied in analysis of conductometric titration data and like other linear models, the method needs a calibration step, where the relationship between the conductometric titration data 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 conductometric titration data. The basic concept of PLS regression was originally developed by Wold [11,12] and application of PLS in chemical data have been discussed by several workers [13–16]. In addition, several multicomponent determinations based on the application of these methods to chemical data have been reported [17–21].

Orthogonal signal correction (OSC) was introduced by Wold et al. [22] to remove systematic variation from the response matrix \mathbf{X} that is unrelated, or orthogonal, to the property matrix. Therefore, one can be certain that important information regarding the analyte is retained. Since then, several groups [23–29] have published various OSC algorithms in an attempt to reduce model complexity by removing orthogonal components from the signal. Recently, multicomponent determinations based on the application of OSC-PLS method to spectrophotometric data have been published [21,22].

These requirements fit the description of structured noise in \mathbf{X} . Thus the OSC filter can be used as a preprocessing step prior to latent variable regression modeling, e.g. PLS, to remove the structured noise in \mathbf{X} . The general, single-component OSC model of \mathbf{X} can be expressed by:

$$\mathbf{X} = \mathbf{t}_{\text{osc}}\mathbf{p}_{\text{osc}}^T + \mathbf{X}'$$

where $\mathbf{t}_{\text{osc}} = \mathbf{X}\mathbf{w}_{\text{osc}}$ and $\mathbf{Y}\mathbf{t}_{\text{osc}}^T = 0$. Here, \mathbf{t}_{osc} , \mathbf{p}_{osc} and \mathbf{w}_{osc} represent the single OSC component. \mathbf{X}' is the OSC-filtered matrix subsequently used in the latent variable regression model. More than one OSC component can be identified and removed from \mathbf{X} . For additional OSC components the filter is applied to the \mathbf{X}' matrix. The OSC component is similar to the standard PLS component, as it has two sets of loading vectors, but with the difference that the score vector \mathbf{t}_{osc} is orthogonal to \mathbf{Y} . Comparisons between the results of different OSC filters are often made with regard to the number of OSC components removed. However, such comparisons are difficult to make, because one OSC component can be derived from different multicomponent prediction models.

This paper describes a simple, facile and efficient analytical method, for the first time to our knowledge, for simultaneous determination of acetic acid, monochloroacetic acid and trichloroacetic acid using conductometric titration data and multivariate calibration techniques (partial least squares) with preprocessing by orthogonal signal correction. The aim of this work is to propose orthogonal signal correction-partial least squares (OSC-PLS) method to resolve ternary mixtures of acetic acid, monochloroacetic acid and trichloroacetic acid in synthetic mixtures without prior separation.

2. Experimental

2.1. Reagents and standards solutions

All the chemicals used were of analytical reagent grade, sub-boiling, distilled water was used throughout. Stock acetic acid, monochloroacetic acid and trichloroacetic acid solutions of 0.01 M and hydroxide sodium solution 0.05 M (all chemicals are purchased from Fluka) were prepared. Standards of working solution were made by appropriate dilution daily as required.

2.2. Instrumental and software

The conductometric titrations were carried out in a double walled cell and the temperature kept constant using water bath circulating system. The conductance was measured by a digital conductometer (Metrohm, model 712) equipped with a Pt plat (Metrohm, model) electrode using a DOSIMAT (model 712) as automatic titrator. The data manipulation have done by a Pentium IV (256 Mb RAM) microcomputer using MATLAB software, version 6.5 (The Mathworks). OSC and PLS calculus were carried out using “PLS-Toolbox”, version 2.0 (Eigenvector Company).

2.3. Procedure

In a typical titration, suitable amounts of an individual acid or acids mixtures were placed in a 100 ml vessel and diluted to 50 ml with distilled water. While stirring, the solution monotonically titrated with a stepped addition of 0.05 M NaOH solution using a DOSIMAT (model 712). The conductance of solution was recorded after addition of 0.1 ml of titrant, and 50 data points were recorded for each titration curve. This is very important that the volume added be in equal distance then could be used as measured variables to build PLS calibration model. In entire titration the temperature kept constant at $25.0\text{ }^{\circ}\text{C} \pm 0.1$.

3. Results and discussion

The acids used in this study are chemically related compounds and they have very close acidity constants. The pK_a of acetic acid, monochloroacetic acid and trichloroacetic acid are 4.76, 2.87 and 0.89, respectively. Fig. 1 shows the conductometric titration curves of these acids and their mixtures. It is obvious that the neutralization steps in the titration curves of these three acids are overlapped seriously. For overcoming this drawback for simultaneous determination and removing the interference effects of one component in the presence of others a PLS-1(-1 means PLS algorithm used here can model the concentration of each component separately and finally three separate calibration model were obtained for three components) multivariate calibration approach applied. In addition, the present study shows that OSC can be a good method to remove systematic variation from the response matrix \mathbf{X} that is unrelated, or orthogonal, to the property matrix \mathbf{Y} . The several linear and non-linear operators as scaling of the response variable, \mathbf{Y} , were checked to enhance the linear relationship between conductance and concentration

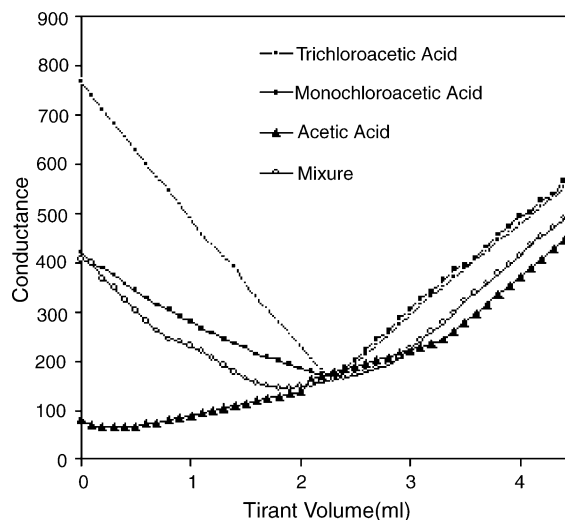


Fig. 1. Titration curves for acetic acid, monochloroacetic acid and trichloroacetic acid and their mixtures with sodium hydroxide solution.

of acids in calibration model building. It was found the square of the concentration shows the minimum values of model residuals. The difference of the RMSEP was significant at 99% of confidence level using Student's *t*-test. Then in all the subsequent steps we used the squares of the concentration values instead of original concentration values.

3.1. Calibration and validation

Two sets of standard solutions were prepared. The calibration set contains 16 standard solutions. The compositions of the calibration mixtures were selected according to (3, 4) orthogonal design [30]. In Table 1, the compositions of the ternary mixtures used in the calibration matrices are summarized. For prediction set, eight mixtures were prepared according procedure section (see Table 2). To ensure that the prediction or synthetic samples

Table 1

Concentration data of the different mixtures used in the calibration set for the determination of acetic acid, monochloroacetic acid and trichloroacetic acid

Solution number	Concentration of acid (mM)		
	Acetic acid	Monochloroacetic acid	Trichloroacetic acid
M1	0.50	0.60	0.80
M2	1.00	1.20	2.20
M3	1.00	1.80	1.60
M4	1.50	1.20	0.80
M5	1.00	0.60	2.20
M6	0.50	1.80	2.20
M7	1.50	1.80	2.80
M8	1.50	2.40	2.20
M9	2.00	1.80	0.80
M10	1.50	0.60	2.80
M11	0.50	2.40	2.80
M12	2.00	2.40	1.60
M13	2.00	1.20	2.80
M14	1.00	2.40	0.80
M15	2.00	0.60	1.60
M16	0.50	1.20	1.60

Table 2
Added and found results of synthetic mixtures of acetic acid, monochloroacetic acid and trichloroacetic acid mixtures by PLS and OSC-PLS.

Prediction mixtures	Added ^a			PLS						OSC-PLS					
				Found			Relative error			Found			Relative error		
	A	M	T	A	M	T	A	M	T	A	M	T	A	M	T
P1	0.90	1.19	1.50	1.00	2.10	1.30	11.1	10.0	-13.3	0.85	2.00	1.40	-5.5	5.0	-6.6
P2	1.15	1.16	1.70	1.30	1.70	1.90	13.0	6.2	11.7	1.10	1.50	1.80	-4.3	-6.2	5.8
P3	1.52	1.80	0.90	1.40	1.70	0.80	-7.8	-5.5	-11.1	1.50	1.70	0.90	-1.3	5.5	0.0
P4	1.10	1.50	1.70	1.00	1.00	1.90	-9.0	-33.3	11.7	1.20	1.70	1.8	-9.0	13.3	5.8
P5	1.60	1.20	0.85	1.40	1.00	1.00	-12.5	-16.6	17.6	1.70	1.10	0.80	-6.2	-8.3	-5.8
P6	1.30	1.20	0.85	1.10	0.70	1.50	-15.3	-14.6	15.3	1.20	0.90	1.40	-7.6	9.7	7.6
P7	0.90	1.20	1.20	1.10	1.00	1.40	22.2	-16.6	16.6	0.80	1.20	1.30	-11.1	0.0	8.3
P8	0.80	2.30	0.80	0.95	2.00	1.00	18.7	-13.4	25.0	0.70	2.20	0.90	-7.7	4.7	12.5

^a (A): acetic acid; (M): monochloroacetic acid; (T): trichloroacetic acid.

are in the subspace of training set, the score plot of first principal component versus second one was sketched and all the samples are spanned with the training set scores.

3.2. Preprocessing by orthogonal signal correction

Generally the OSC operate on the scaled data (mean centered and variance scale of the \mathbf{X} and \mathbf{Y}), and it removes the uncorrelated variations of \mathbf{X} with respect to \mathbf{Y} variables. For calibration set the optimum number of OSC components was found one 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 (RMSEP) values than original data. Also, the OSC-filtered data give much simpler calibration models with fewer components than the ones based on original data. The results imply that the OSC method indeed removes information from conductometric titration data that is not necessary for fitting of the \mathbf{Y} -variables. In some cases the OSC method also removes non-linear relationships between \mathbf{X} and \mathbf{Y} . The effect of the OSC on the calibration model can be also seen from the score plots of the PLS and OSC-PLS. This difference in the score plots (which is object map in a reduced multidimensional space) reveals that the OSC removed the orthogonal part of the \mathbf{X} variation to the \mathbf{Y} variables. Now, the geometrical coordinates of the objects in the two-dimensional score plot are similar to the expected values of the concentration of the mixtures solution of calibration samples. The similar trend has been observed previously [22,24,25].

3.3. Selection of 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:

$$\text{PRESS} = \sum (y_i - \hat{y}_i)^2$$

where y_i is the reference concentration for the i th sample and \hat{y}_i represents the estimated concentration. A cross-validation method

was employed to eliminate only one sample at a time and then PLS or OSC-PLS algorithm models the remaining \mathbf{Y} matrix and corresponding \mathbf{X} matrix. 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 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 and Thomas [31] 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 9 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. 2 is shown

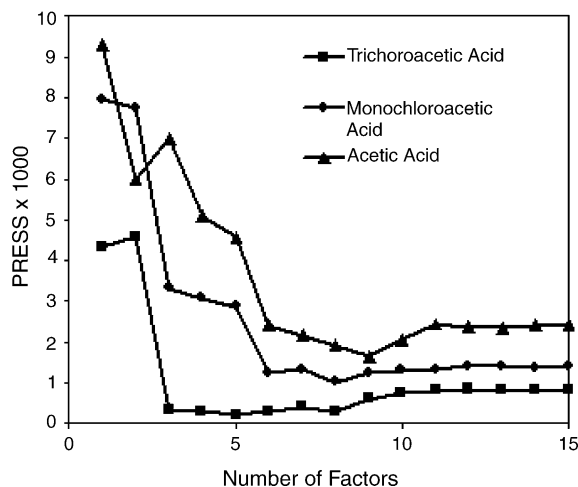


Fig. 2. PRESS vs. number of significant factors. (▲) Acetic acid, (●) monochloroacetic acid and (■) trichloroacetic acid using OSC-PLS regression.

Table 3

Statistical parameters of the optimized matrix using the PLS and OSC-PLS methods to the synthetic mixtures

Parameters	PLS			OSC-PLS		
	Acetic acid	Monochloroacetic acid	Trichloroacetic acid	Acetic acid	Monochloroacetic acid	Trichloroacetic acid
NPC ^a	5	5	5	5	5	4
RMSEP	0.15	0.40	0.18	0.08	0.3	0.08
REP(%)	13.6	18.5	13.6	7.18	12.50	7.00
R ²	0.70	0.88	0.84	0.99	0.93	0.99
R	0.83	0.93	0.92	0.994	0.96	0.994

^a Number of principal components.

the PRESS obtained by optimizing the calibration matrix of the conductometric titration data with OSC-PLS.

3.4. Determination of acetic acid, monochloroacetic acid and trichloroacetic acid in synthetic mixtures

The predictive ability and validation of the calibration model was assessed using eight three-component of acetic acid, monochloroacetic acid and trichloroacetic acid mixtures (their compositions are given in Table 2). The results obtained by applying PLS and OSC-PLS algorithm to eight synthetic samples are listed in Table 2. Table 2 also shows the relative error for prediction series of acetic acid, monochloroacetic acid and trichloroacetic acid mixtures. However, the number of principal components are same for model obtained by using PLS and OSC-PLS algorithms, but as it can be seen, the relative errors of the OSC-PLS based calibration model show significant priority over PLS without OSC filtering model. The plots of the predicted concentration versus actual values are shown in Fig. 3 for acetic acid, monochloroacetic acid and trichloroacetic acid (line equations and R² values are also shown).

3.5. Statistical parameters

For the optimized model three parameters were selected to assess prediction ability of the model for simultaneous determination of acetic acid, monochloroacetic acid and trichloroacetic acid. Root mean squares error of prediction (RMSEP), which is an indication of the average error in the analysis, for each component:

$$\text{RMSEP} = \left[\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \right]^{0.5}$$

The RMSEP values are an estimate of the absolute error of prediction for each component and another useful parameter is the relative error of prediction (REP%) that shows the predictive ability of each component, calculated as:

$$\text{REP}(\%) = \frac{100}{\bar{y}} \left[\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \right]^{0.5}$$

The square of the correlation coefficient (R²), which is indicated the quality of fit of all the data to a straight line is calculated for

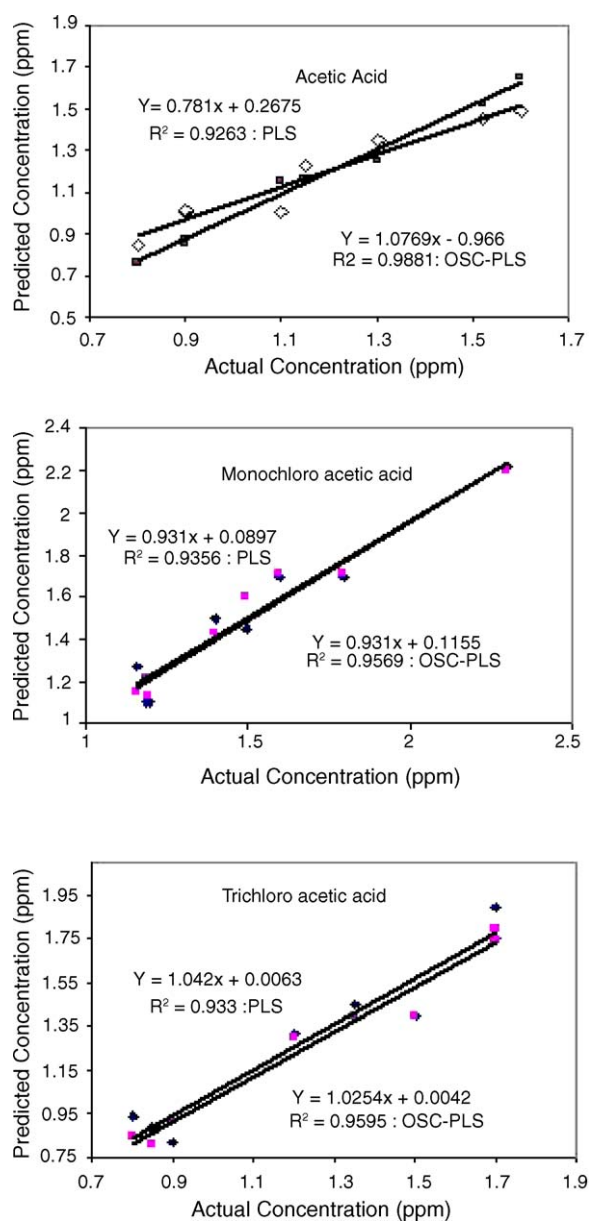


Fig. 3. Predicted concentration vs. actual concentration for three acids in the prediction set. (A): Acetic acid, (M): monochloroacetic acid, (T): trichloroacetic acid and by PLS(◆) and OSC-PLS (◇).

the checking of each calibration, and is calculated as:

$$R^2 = \frac{\sum_{i=1}^n (\hat{y}_i - \bar{y})^2}{\sum_{i=1}^n (y_i - \bar{y})^2}$$

where y_i is the true concentration of the analyte in the sample i . \hat{y}_i represents the estimated concentration of the analyte in the sample i , \bar{y} the mean of the true concentration in the prediction set and n is the total number of sample used in the prediction set. The value of RMSEP, REP(%) and R^2 for acetic acid, monochloroacetic acid and trichloroacetic acid summarized in Table 3. The results of the Table 3 clearly show the successful application of the OSC filtering method. To simplify the comparison the RMSEP and REP% and R^2 values are shown for the same principal components of the PLS and OSC-PLS algorithm. The three statistical parameters of OSC-PLS algorithm are drastically smaller than the corresponding parameters for the PLS algorithm.

4. Conclusions

Acetic acid, monochloroacetic acid and trichloroacetic acid mixture is an extremely difficult complex system due to high degree of overlapping observed among the conductometric titration data. For overcoming the drawback of this interference the PLS multivariate calibration approach is applied. In addition, the present study shows that OSC can be a good preprocessing method to remove systematic variation from the response matrix \mathbf{X} that is unrelated, or orthogonal, to the property matrix \mathbf{Y} . The good agreement between calculated and experimental concentrations of three components clearly demonstrate successful application of this procedure for the simultaneous determination of acetic acid, monochloroacetic acid and trichloroacetic acid, without tedious pretreatments in synthetic mixtures.

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