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Short communication

Application of attenuated total reflectance Fourier transform infrared spectrometry to the determination of sodium percarbonate in washing powder detergent

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Abstract

In this paper, a novel and precise analytical procedure has been developed for quantitative determination of sodium percarbonate (SPC) in washing powder. The method is based on the partial least squares (PLS) treatment of data obtained by attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectrometry in wavenumber region of 1435–1342 cm^{-1}. The statistical parameters such as R^2, RSD, SEC and SECV have been evaluated, and number of factors, number of scan and the resolution have been optimized. In this method R^2 and RSD for five independent analyses of a 0.552 g per 100 g solution of SPC, SEC for 10 standard samples and SECV for five validation samples were 0.998, 1.011, 0.002 and 0.039 respectively.

Results obtained for six different commercial washing powders compared well with those obtained with a standard method.

Keywords: Sodium percarbonate; Washing powder; Spectrometry; PLS; ATR FT-IR

1. Introduction

SPC is a solid per-oxygen compounds with exceptional storage stability and no shock sensitivity which is also environmentally friendly. It is cheap, non-toxic and readily available, being produced mainly as solid ingredient of domestic washing formulation, in which it acts as a source of H_2O_2 in solution for stain bleaching [1–4].

FT-IR spectrometry is a fast analytical technique and provides very interesting qualitative and quantitative information [5–9]. In this way the use of attenuated total reflectance (ATR) measurements improves the use of the mid-IR by simplifying sample handling and avoiding measurement problems commonly found in transmission cells such as filling and cleaning or variation of the pathlength due to window wear [10]. Also, ATR is an appropriate technique for aqueous samples because the evanescent field penetrates only a very short distance, of the order of the wavelength of the incident IR radiation, into the aqueous solution [11].

The abilities of different chemometrics methods to resolve mixture of different compounds whose signals are overlapped have been widely utilized. The main advantage of multivariate analysis using PLS calibration is the speed of the determination for the components in mixture avoiding the need for a prior separation that is otherwise necessary owing to the overlapping of signals [12]. Among chemometrics method PLS frequently have been used because of the quality of the calibration models obtained, the ease of its implementation and the availability of software [13–16].

Powder detergents are one of the most famous and widely applied products that contain SPC. SPC is known as a bleaching or oxidizing agent.

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The standard method for determination of SPC is ISO number 4321 which is based on titrimetric method. This procedure is time-consuming.

This paper deals with the direct determination of SPC at the presence of the related matrix of washing powder, e.g. sodium carboxy methyl cellulose (CMC), linear alkyl benzene sulfonate (LABS), sodium sulfate (SS), sodium silicate (S-Si) and sodium tripolyphosphate (STPP), using ATR FT-IR method.

2. Experimental

2.1. Apparatus and software

A Magna 550 FT-IR spectrometer (Nicolet, Madison, WI, USA) equipped with a DTGS detector, an Ever-Glo source and a CsI beamsplitter, was employed for spectral measurements with a nominal resolution between 0.5 and 32 cm^{-1}. The FT-IR spectra of liquid samples were obtained with a horizontal model Spectra Tech ATR cell equipped with a 45° ZnSe trough plate. Omnic software was used to control instrument for data acquisition. The Omnic QuantIR software from Nicolet was used to process the absorbance data using a PLS algorithm.

2.2. Reagents and procedure

All reagents were of analytical grade and distilled water was used as solvent through the procedure. To optimize and evaluate the prediction capability of the PLS-IR model, standard solutions of SPC were made up in aqueous solution in various concentrations between 0.104 and 1.001% (g per 100 g). Also compounds such as sodium carboxymethyl cellulose (CMC), linear alkylbenzene sulfonate (LABS), sodium sulfate (SS), sodium silicate (S-Si) and sodium tripolyphosphate (STPP) were added to each standard solution to make the matrix of these solutions similar to the matrix of washing powder. The concentration of these compounds, SS, CMC, STPP, LABS, and S-Si in all 15 standard solutions were kept constant and equal to 0.62, 0.07, 0.67, 0.46 and 41% (w/w) respectively. Ten standards were used to set up the PLS models and five other standards were employed to evaluate these models.

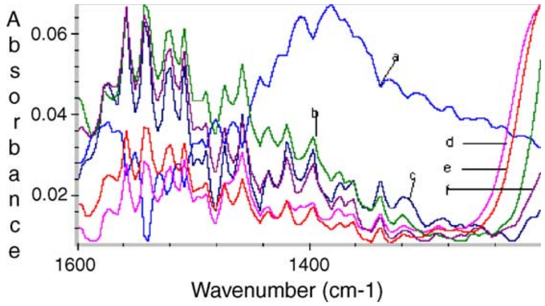

Fig. 1. The FT-IR spectra of: (a) SPC, (b) SS, (c) CMC, (d) LABS, (e) STPP and (f) S-Si, using solvent as reference.

For several years, titrimetric method has been used for determination of SPC in washing powder detergent (ISO 4321). Also, in the present investigation in order to evaluate the results obtained by the proposed ATR FT-IR method, some samples were analyzed by this standard method.

The ATR FT-IR spectra were obtained in the 1600–1200 cm^{-1} spectra range employing Happ-Genzel apodization and with the use of 10 scans and a nominal resolution of 8 cm^{-1}. The ATR FT-IR spectra of aqueous solution of SPC and each of the matrix compounds using solvent as a reference are shown in Fig. 1.

Fifteen standard solutions were prepared by dissolving appropriate amounts of standard SPC and the related matrixes in distilled water, so that the concentration of the SPC varies between 0.104 and 1.001% (g per 100 g), as shown in Table 1, but the concentrations of the related matrixes in all these standard solutions were kept constant. Fig. 2 shows the spectra of these standard solutions using water as reference.

Table 1
Concentration of SPC applied in calibration (samples nos. 1–10) and validation (samples nos. 11–15) set

Sample	Actual concentration (g per 100 g)	Prediction concentration (g per 100 g) (PLS)	Prediction concentration (g per 100 g) (CLS)
1	0.104	0.106	0.081
2	0.204	0.202	0.263
3	0.296	0.295	0.280
4	0.401	0.401	0.570
5	0.491	0.492	0.526
6	0.600	0.601	0.406
7	0.694	0.694	0.590
8	0.793	0.795	0.672
9	0.900	0.900	1.109
10	1.001	0.999	1.026
11	0.232	0.233	0.237
12	0.477	0.475	0.481
13	0.761	0.759	0.820
14	0.830	0.831	0.801
15	0.980	0.977	1.149

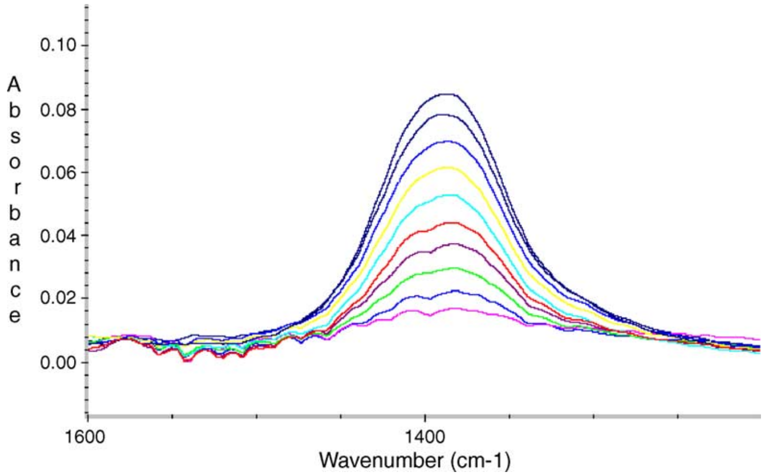

Fig. 2. The FT-IR spectra of standard solutions of SPC with concentrations of 0.104–1.001 g per 100 g containing different amount of other related matrix, using solvent as reference.

3. Results and discussion

SPC, CMC, LABS, SS, S-Si and STPP are the main components of the iranian commercial detergents. They are used in the detergent as oxidizing (SPC), antiredeposition (CMC), cleaning (LABS), filler (SS), builder (S-Si) and water softening (STPP) agents [17].

The spectra of SPC in Fig. 1, shows one main absorbance band at 1435–1342 cm^{-1}. Also in this figure, CMC and S-Si show appreciable absorbance at this spectral region of 1435–1342 cm^{-1} and overlap with SPC band. On the other hand, Fig. 2 shows a direct relationship between the absorbance at 1435–1342 cm^{-1} and the concentration of the standard solutions. However if one can overcome the problem of overlapping the SPC band with the bands of other related matrix, the quantitative analysis of SPC in commercial washing detergent can be carried out using these absorbance spectra.

Multivariate calibrations are useful tools to be used in spectral analysis in order to overcome the spectral overlapping and to improve the precision and the predictive ability of the FT-IR spectrometry. With the aim of quantitative analysis of SPC in powder detergent, the PLS multivariate model was applied with the absorption spectra data. Spectral information was mean centered prior to PLS data treatment.

The unique way to verify that one calibration model works well is to take new samples and predict them by the model. However several ways for validation, including leverage correction, cross-validation using small data set, leave-one out cross-validation and testing new samples, have been proposed [18]. In this work, the leave-one out cross-validation using small data set was used. The basis of this method is that, the predicted ability of a model formed on part of dataset can be tested out by how well it predicts the reminder of dataset. However, the first 10 standard solutions (samples nos. 1–10 of Table 1) were used to setup the calibration curve and then by performing the leave-one out cross-validation process, the concentrations of these solutions were predicted. The predicted results are shown in Table 1. This calibration model was tested by varying the number of PLS factors from 1 to 6 in order to optimize the models.

To select the optimum number of factors in PLS algorithm, the cross-validation method, leaving out one sample at a time, was used. The prediction error sum of squares (PRESS) was calculated each time a new factor was added giving rise to different PLS models. One reasonable choice for the optimum number of factors would be that number (h*) which yielded the minimum PRESS. However, the best calibration models were obtained for the set of spectra with 3 PLS factor. With this optimum number of factors, standard error of calibration (SEC) was calculated for these 10 standard samples using equation:

$$\mathrm{SEC} = \sqrt{\frac{\sum_{i=1}^{n}(y_{\mathrm{k}i} - y_{\mathrm{p}i})^2}{n - f - 1}}$$

in which, n is the number of samples, y_k the known concentration, y_p the predicted concentration and f the number of factors. SEC was 0.002. Relative standard deviation (RSD) for five independent analysis of a 0.552 g per 100 g solution of SPC and square correlation of coefficient (R^2) of the calibration cure were calculated. RSD and R^2 were 1.011 and 0.998 respectively.

Different spectral regions were evaluated by performing PLS calibration method and the spectral wavenumber of 1435–1342 cm^{-1} was selected as most convenient spectral region. Also in order to ensure that this calibration model would provide accurate prediction, the last five samples (samples nos. 11–15 of Table 1) were proposed as validation set and their concentration were predicted by using the calibration curve. The results are shown in Table 1. Standard error of cross-validation (SECV) was also calculated for these five

Table 2
Determination SPC in commercial washing powder detergents by standard and proposed methods

Sample	Proposed method (g per 100 g)	Standard method (g per 100 g)[a]
1	0.237	0.242
2	0.715	0.714
3	0.896	0.892
4	10.201	9.972
5	8.897	9.140
6	11.290	10.984

[a] Standard methods of SPC is ISO 4321.

validation samples using equation:

$$\mathrm{SECV} = \sqrt{\frac{\sum_{i=1}^{n}(y_{\mathrm{k}i} - y_{\mathrm{p}i})^2}{n}}$$

The SECV was 0.039.

Finally the absorbances from the maximum in the spectral range of 1435–1342 cm^{-1} were regressed against concentrations of standard and validation set using classical least squares (CLS) regression to find the better regression model. The results of this evaluation are also shown in Table 1. With PLS method, more accurate results were obtained and because of that, the PLS regression was selected as better calibration model.

3.1. *Real sample analysis*

Six commercial washing powder detergents supplied by three persian producer, were analyzed by proposed method and the concentration of SPC in these real samples were calculated. In order to evaluate the accuracy of the proposed method, these six real samples were also analyzed by a standard method (ISO 4321). The results are shown in Table 2. Samples nos. 1–3 were prepared from Tolypers company. Trade names of this hand washing powder are Darya 1, Darya 2 and Darya 3. Tolypers company also supplied machine washing powder samples nos. 4 and 5 with brand name of Shoma and Shoma+, respectively .The last sample was purchased from Behdad company with the name of Tage. Generally good agreement was found between the concentration of SPC using the standard and proposed method.

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