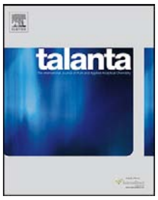
Talanta 81 (2010) 799–804

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta



Combining the least correlation design, wavelet packet transform and correlation coefficient test to reduce the size of calibration set for NIR quantitative analysis in multi-component systems

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ARTICLE INFO

Article history:
Received 23 September 2009
Received in revised form 10 January 2010
Accepted 13 January 2010
Available online 21 January 2010

Keywords:
Wavelet packet transform (WPT)
The least correlation design
Correlation coefficient test (*r*-test)
Multi-component system
Partial least squares (PLS)
Small-scale calibration set
Near-infrared spectroscopy (NIR)

ABSTRACT

The paper focuses on solving a common and important problem of NIR quantitative analysis in multi-component systems: how to significantly reduce the size of the calibration set while not impairing the predictive precision. To cope with the problem orthogonal discrete wavelet packet transform (WPT), the least correlation design and correlation coefficient test (*r*-test) have been combined together. As three examples, a two-component carbon tetrachloride system with 21 calibration samples, a two-component aqueous system with 21 calibration samples, and a two-component aqueous system with 41 calibration samples have been treated with the proposed strategy, respectively. In comparison with some previous methods based on much more calibration samples, the results out of the strategy showed that the predictive ability was not obviously decreased for the first system while being clearly strengthened for the second one, and the predictive precision out of the third one was even satisfactory enough for most cases of quantitative analysis. In addition, all important factors and parameters related to our strategy are discussed in detail.

1. Introduction

In a multi-component system, the NIR spectra of its components usually overlap, and what is perhaps worse, the spectral effect of one component varies not only with the concentration of the component itself but probably with concentrations of other components because of the interaction among components in the system. These phenomena often mean that a number of concentration levels are indispensable to each component and each level of one component needs a chance to be mixed with each level of other components in the calibration samples. That is to say, a large-scale calibration set based on the full experimental design is commonly demanded.

Of course, not all multi-component systems need a large-scale calibration set, in particular if concentrations of each components in the system vary in a small range or only a rough prediction is satisfactory so that several concentration levels of each component in the calibration set are enough [1–4]. But for a multi-component system with wide concentration range, it is impossible to make precise predictions with this simple way because the larger the concentration interval in the calibration set is, the more prediction error will be.

This difficulty may not be alleviated even by common techniques of experimental design, such as factorial design, half-fraction factorial design, or popular orthogonal design, because of the different situations. These techniques aiming at effectively finding out some special points like optimal process condition for chemical industry may not work well in our cases where the precise predictions are required within the entire concentration range rather than just near a certain concentration point. Furthermore, even using these designs the number of calibration samples is usually still large, for instance, with orthogonal design at least 400 (20^2) samples are demanded for a multi-component system when each component needs 20 concentration levels, respectively (a moderate requirement for NIR quantitative analysis).

In our former research [5], an improved method based on random experimental design, discrete wavelet transform (DWT) and correlation coefficient test (*r*-test) has been suggested to cope with the problem. The method works very well in some cases, such as carbon tetrachloride system where the NIR information is abundant, but “is not enough satisfactory in most cases” like aqueous system where the NIR information is scarce. Therefore, “other experimental and/or chemometrics improvement should be taken further” [5].

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doi:10.1016/j.talanta.2010.01.018

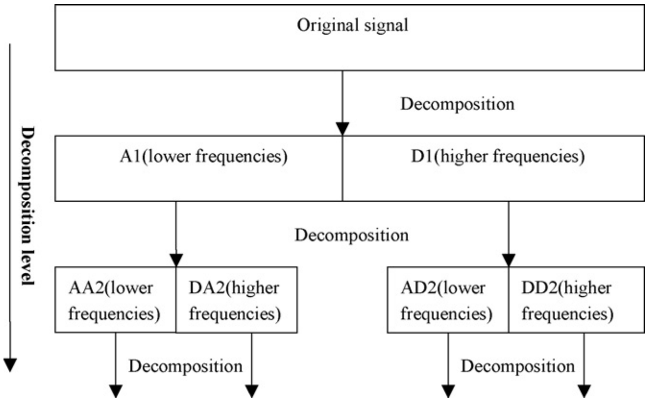

Fig. 1. WPT decomposition.

This paper is just one of follow-up attempts. Its purpose – reducing the size of calibration set without at the price of predictive precision for NIR quantitative analysis in a multi-component system, and major idea – extracting NIR features merely related to one component but irrelevant to all other components in order to construct a multivariate calibration model for the component, are the same as the former research, but it tries to improve the experimental design and replace the DWT with WPT for achieving the purpose better.

2. Theory and algorithm

2.1. Wavelet packet transform (WPT)

Discrete wavelet transform (DWT) decomposes a signal in time domain into a series of wavelet coefficients (namely, approximation coefficients and detail coefficients) in a new time-frequency space. Consequently, some features inconspicuous or overlapping in the initial domain might become obvious or separate in the new space [6,7]. One major shortage of DWT is that there is lower frequency resolution for higher frequencies, and lower time resolution for low frequencies, because only lower frequencies are decomposed further. This made DWT be suitable for most signals, but for a smooth signal like NIR spectra, sometimes it is difficult for DWT to provide both appropriate time resolution as well as frequency resolution simultaneously. In order to overcome this problem WPT [8,9] has been developed. The fundamental of WPT is largely similar to that of DWT except that the part of higher frequencies is also decomposed continuously. Therefore, WPT is more flexible to balance the time resolution and frequency resolution than DWT, and accordingly extract features better or separate the overlapping information more effectively from the original signal in some cases.

Fig. 1 succinctly describes the procedure of WPT decomposition from a standpoint of signal processing. At first an original signal is decomposed into two parts – lower frequencies and higher frequencies – on the first decomposition level. In the step, the information in lower frequency part is transformed into approximation coefficients (A1), while other information in higher frequencies is depicted by detail coefficients (D1). Then, the part of higher frequencies as well as the part of lower frequencies is decomposed respectively on the second decomposition level. This procedure can be carried out up to the maximum decomposition level.

2.2. Treating NIR spectra with WPT

The same WPT procedure can be conveniently implemented for a NIR spectrum as long as the time domain is replaced by the wavelength (or wavenumber) domain. In fact, WPT has been applied to NIR analysis, such as transfer of calibration model [10], classification [11], signal denoising, correction or database compression [12,13], and a few reports were also concerned with the application of WPT to multivariate calibration [14]. But to our knowledge, little effort has been made to study the purpose mentioned in the introduction section of the paper with WPT.

In the view of information, the information contained in the original signal is equal to A1 + D1, A1 + AD2 + DD2, AA2 + DA2 + D1, or AA2 + DA2 + AD2 + DD2 in Fig. 1. That is to say, an original signal could be decomposed in different ways through WPT, and consequently it is necessary to find an optimal decomposition mode (namely, wavelet packet decomposition tree) in terms of a convenient criterion. In general, Shannon entropy that describes information-related property of the signal is chosen as the criterion. The best decomposition tree is the one with minimum entropy, or in other words, the one whose regularity or information approaches the maximum.

Finally, since WPT transforms a signal linearly from its original domain to a new domain without prejudice, it is not necessary to reconstruct the original signal with processed wavelet coefficients, and the multivariate calibration model could be built between the concentrations of components and these coefficients.

2.3. Criterion for variable selection and the least correlation design

After WPT, all information of a NIR spectrum is transformed into a series of wavelet coefficients. Now what we need is to determine which coefficients are related merely to the concentration of a particular component, while insusceptible to the concentration variation of all other components. Such coefficients can be used as suitable variables to build a multivariate calibration model for predicting the concentration of this component. A variety of chemometrics methods have been developed to select suitable variables for model construction, from stepwise regression analysis (SRA) [15], uninformative variables elimination (UVE) [16–19], genetic algorithm (GA) [20–22], simulated annealing algorithm (SAA) [23], interval partial least squares (iPLS) [24], to moving window partial least squares regression (MWPLSR) [25,26]. These methods work very well in their own cases, but may not be appropriate for the case of our concern, since they mainly focus on selecting variables containing most information of the concerned component while paying no special attention to the correlation between these variables selected and other components.

In our former paper [5], we suggested a method based on random experimental design and correlation coefficient test (*r*-test) to select wavelet coefficients for building multivariate calibration model. The crucial idea of the strategy is that through the correlation coefficients between one wavelet coefficient and the concentration of every component in the calibration set we could determine whether the wavelet coefficient are related merely to the concentration of a particular component, while insusceptible to the concentration variation of all other components. For making the idea feasible, in calibration samples the concentration of one component should be irrelevant to that of any other component. Consequently, in the former research, the concentration of every component in every calibration sample is arranged randomly.

Although this random experimental design can effectively reduce the correlation among components to a certain degree, in general this kind of relationship is not the least. Therefore, in this paper, the least correlation design is proposed to supplant random experimental design. In the least correlation design: (1) the concentration of any component in one calibration sample should differ from the concentration of this component in all other samples if possible; (2) for the same component, the concentration interval should be equal; and (3) in the calibration set all components have

Table 1
Correlation coefficients between two variables when they are arranged according to the least experimental design.

LV	2	3	4	12	15
CC	1.0000	0.5000	0.0000	0.0000	0.0000
MCC	1.0000	0.6071	0.4086	0.0902	0.0655
LV	21	24	30	40	50
CC	0.0000	0.0000	0.0000	0.0000	0.0000
MCC	0.0380	0.0321	0.0242	0.0159	0.0120

LV: level or dimension of each variable; CC: the correlation coefficient between the two variables when the values of the two variables are exact; MCC: the mean of the absolute value of 1000 correlation coefficients between the two variables when the values of the two variables vibrate in the way of normal distribution.

the same number of concentration levels. With this design, not only could the number of calibration samples be significantly reduced, but it is possible to select suitable variables (e.g., wavelet coefficients) according to *r*-test because it is unlikely for one variable to correlate largely with concentrations of more than one component at the same time. If a wavelet coefficient out of calibration samples greatly correlates with the concentration of one component, while being obviously irrelevant to that of any other component, it is just the variable that we are looking for. In statistics *r*-test is commonly used to determine the correlation between two variables or vectors. If $|r| \le R_{0.05}\ (n-2)$, then we think the correlation between them is feeble; and if $|r| > R_{0.01}\ (n-2)$, the two variables are obviously related. Here, *r* is the correlation coefficient; R_α can be simply inferred from *F*-test: $R_\alpha\ (n-2) = \{F_\alpha\ (1,\ n-2)/[F_\alpha\ (1,\ n-2)+n-2]\}^{0.5}$; α is the significance level; and *n* is the level or dimension of the two variables.

2.4. The number of the calibration samples required

Another crucial parameter that should be decided is the appropriate number of the calibration samples. From CC of Table 1, one could know that it is possible for the least correlation design to make the concentrations of two components completely irrelevant if they both have more than three levels. For example, if all components have 4 concentration levels in a two-component system, the concentration arrange according to the least correlation design is {3, 4} in the first sample, {1, 3} in the second sample, {2, 1} in the third sample, and {4, 2} in the fourth sample. And accordingly the correlation coefficient between concentrations of the two components, namely the two concentration vectors [3,1,2,4] and [4,3,1,2], is zero (here, {3, 4}, {1, 3}, {2, 1}, and {4, 2} are concentrations of the two components in each calibration sample, respectively). However, this does not mean that four levels are enough for NIR quantitative analysis, because of experimental errors and possible nonlinearity between concentration and spectral feature (as discussion above, the suitable variables are chosen according to the correlation coefficient between the concentration and the wavelet coefficients of spectra). This could be clearly observed from MCC in Table 1, where the exact values of concentrations are replaced by values vibrating according to a normal distribution (the mean of the distribution function is the exact value, and the standard deviation of the normal distribution is assumed as 10,000), and MCC is the mean of the absolute value of 1000 correlation coefficients between the concentrations that vibrate around their own exact values respectively. Therefore, 21–40 concentration levels (namely, 21–40 calibration samples) are usually needed in the proposed strategy, for the MCC is less than 0.05, and more concentration levels (namely, calibration samples) cannot reduce MCC obviously. On the other hand, such a calibration set is relatively small and generally necessary even for multivariate calibration model construction in a one-component system.

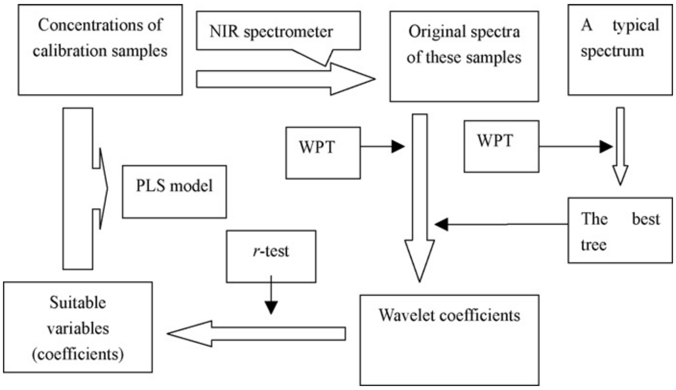

Fig. 2. An overview of steps involved in data processing.

Comparing the CC and MCC in Table 1 of this paper with the MCC in Table 1 of our former paper [5], one would discover that the random experimental design cannot decrease the correlation between the concentration of one component and that of another component furthest as the least experimental design, and as a result, the former design demands more calibration samples (30–50 samples) than the latter one.

2.5. Overview of data processing

Firstly, 21–40 samples are prepared as a calibration set according to the least correlation design, and a typical NIR spectrum (usually the spectrum of the sample whose concentrations are nearly the median of the entire calibration set) are decomposed by a kind of discrete wavelets to find the best decomposition tree in terms of Shannon entropy. All spectra of the calibration samples are decomposed by the same discrete wavelet according to the same decomposition tree. After discarding the detail coefficients of the highest frequency (commonly resulted from the noise of spectrometer) to save computing time, the correlation coefficient between every wavelet coefficient and the concentration of each component is obtained respectively. Then *r*-test is carried out to select suitable wavelet coefficients as suitable variables for one component. And finally based on these variables and the concentration of the component, a partial least squares (PLS) model is constructed in a conventional leave-one-out cross-validation way for predicting the amount of the component in the multi-component system. It is worth noting that in the above process, denoising, baseline correction and database compression have also been implemented at the same time. The total procedure is succinctly depicted in Fig. 2.

3. Experimental

Two two-component systems, aniline–acetone carbon tetrachloride solution and aniline–acetone water solution, have been studied with the proposed strategy. For each system, according to the above least correlation design, 21 samples in which the concentration of every component ranged from 0.5% to 5.0% (v/v) at intervals of 0.2250%, respectively, were prepared as a calibration set (see Table 2), and this arrangement made the correlation coefficient between concentrations of the two components are zero if there was not any experimental error. Other 15 samples within 0.5–5.0% were prepared as the prediction set for the two system, respectively. Spectra were all recorded with a Nicolet Nexus 870 FT-IR spectrometer under the same conditions, i.e., resolution of NIR: 4000 cm^{-1}; number of scans: 32; range of scans: 4000–10,000 cm^{-1}, the thickness of quartz-cell: 1 mm; and temperature: 273.15 K. All spectra were difference spectra, namely, subtracting the spectra of solvent away from the sample spectra

Table 2
The concentrations of each component in the 21 calibration samples according to the least correlation design.

Sample	1	2	3	4	5	6	7
C_{an} %	4.1000	2.7500	0.5000	1.1750	3.6500	2.0750	3.2000
C_{ac} %	5.0000	0.7250	2.3000	3.2000	3.8750	2.0750	1.4000
Sample	8	9	10	11	12	13	14
C_{an} %	0.9500	5.0000	1.8500	4.5500	4.3250	4.7750	3.4250
C_{ac} %	1.6250	0.5000	3.4250	4.1000	1.8500	3.6500	2.9750
Sample	15	16	17	18	19	20	21
C_{an} %	0.7250	1.6250	2.3000	2.9750	3.8750	2.5250	1.4000
C_{ac} %	1.1750	4.7750	2.5250	2.7500	0.9500	4.5500	4.3250

C_{an}: the concentration of aniline; C_{ac}: the concentration of acetone.

for obtaining the "pure" spectral effect of the solutes. By the way, these experiments are the same as our former work [5], except that the concentration interval of each component in the calibration set was doubled (in our former work, the concentration interval was 0.1125%, and the calibration set had 41 samples), and consequently its calibration samples were reduced from 41 to 21.

For comparison, 100 samples of aniline–acetone carbon tetrachloride solution as well as 100 samples of aniline–acetone water solution ranging from 0.5% to 5.0% (v/v) at intervals of 0.5% were prepared as other two calibration sets in terms of the full experimental design, and their spectra were obtained in the same way.

Finally, the fifth calibration set with 41 water solution samples based on the least correlation design was also prepared for predicting aqueous aniline–acetone system more exactly.

All algorithms required in this paper were written with MATLAB 7.0 and performed on a personal computer. The steps of the WPT were carried out with the Wavelet Toolbox 3.0 in MATLAB 7.0.

4. Results and discussion

Informative wavebands of carbon tetrachloride system was 4000–7000 cm^{-1} (absorbance within about 8300–8900 cm^{-1} of the second overtones was relatively lower, and not considered in the study), while 4300–4800 cm^{-1} and 5400–6200 cm^{-1} were selected for aqueous system. Within these wavenumber ranges, nine kinds of orthogonal discrete wavelet (db2, db4, db6, coif1, coif3, coif5, sym2, sym4 and sym8) have been tried in the study. Their results were roughly the same, and the db4 was somewhat better than other wavelets for carbon tetrachloride system, while sym8 appeared appropriate slightly for water solution. The best decomposition trees of two systems are shown in Figs. 3 and 4, respectively, which indicate that WPT is superior to DWT in these cases, because in DWT the higher frequency part on every decomposition level would not be decomposed further, and the Shannon entropy out of DWT is definitely more than that out of WPT. By the way, the reason that in carbon tetrachloride system the best WPT decomposition mode could be carried out on more decomposition levels might be that water made some spectral details no longer exist in the aqueous system due to strong solvent effect and the intensive NIR absorbance of water molecules.

The significance levels (α) of r-test are important in the proposed strategy, since changing them could make the selection criterion looser or stricter and consequently affect which wavelet coefficients could enter into constructing PLS model as variables. A larger lower limit of α will make more variables (e.g., wavelet coefficients) containing the information of one component qualified for building the multivariate calibration model for the component, while some variables probably relevant to other components would be also chosen simultaneously; in contrast, a larger upper limit of α will get rid of more wavelet coefficients related to other components, but at the price of losing some information of the component. This influence upon the predictive ability could be seen in Tables 3 and 4,

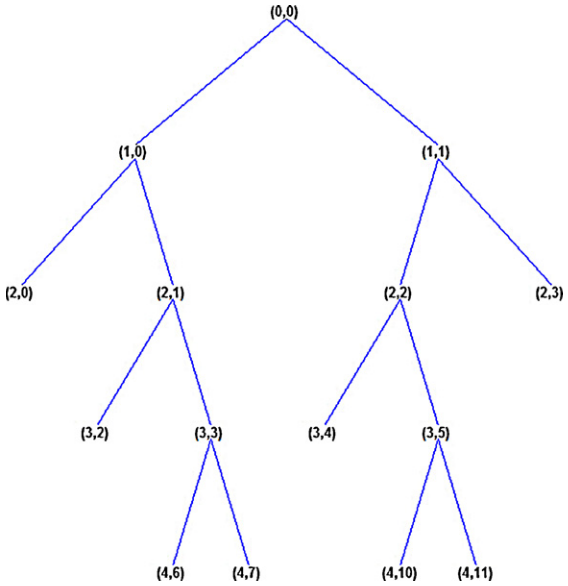

Fig. 3. The best decomposition tree for carbon tetrachloride solution containing 2.9750% aniline and 2.7500% acetone.

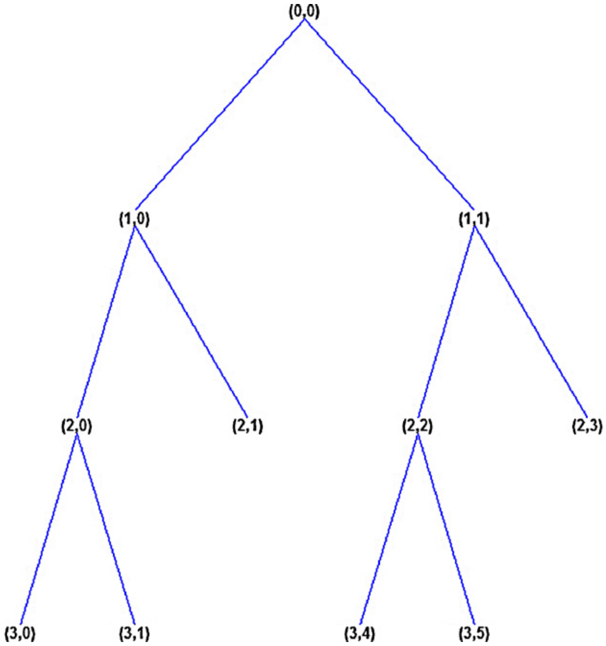

Fig. 4. The best decomposition tree for water solution containing 2.9750% aniline and 2.7500% acetone.

Table 3
Results obtained for the aniline–acetone carbon tetrachloride system with different significance levels of r-test.

Lower and upper limits of α	N of aniline	RMSEP of aniline	N of acetone	RMSEP of acetone
0.0001, 0.25	37	0.1049	35	0.1376
0.0100, 0.25	82	0.0741	67	0.1117
0.0050, 0.10	64	0.0539	46	0.0832
0.0050, 0.25	59	0.0511	46	0.0824
0.0050, 0.30	52	0.0642	40	0.1036

N: the number of variables that are qualified for building multivariate calibration model.

Table 4
Results obtained for aniline–acetone aqueous system with different significance levels of *r*-test.

Lower and upper limits of α	*N* of aniline	RMSEP of aniline	*N* of acetone	RMSEP of acetone
0.0250, 0.25	56	0.1134	50	0.1780
0.0050, 0.25	28	0.0903	37	0.1681
0.0100, 0.10	34	0.0851	41	0.1636
0.0100, 0.25	34	0.0851	41	0.1636
0.0100, 0.30	32	0.0886	41	0.1636

N: the number of variables that are qualified for building multivariate calibration model.

where *N* (the number of variables entering into constructing PLS model) as well as RMSEP (root mean standard error in prediction) was more or less dependent upon the lower and upper limits of significance levels. From these tables, one could also discover that the influence of the lower limit is more obvious that that of the upper one. This is reasonable because the upper limit determines the irrelevance of a wavelet coefficient to one component, whereas through the least correlation design it is unlikely for one coefficient largely related to one component to be still concerned with another component greatly.

According to RMSEP in Tables 3 and 4, the best lower and upper limits of α are 0.0050 and 0.25 for tetrachloride system, while in the aqueous system the best lower limit is 0.01 and the best upper limits is 0.10 or 0.25. This phenomenon can be explained by the fact that in carbon tetrachloride system there was more NIR information, or in other words, more candidate variables than in aqueous system, and accordingly there are still enough variables for multivariate model construction even choosing a stricter criterion as the lower limit. On the other hand, the difference in NIR information of the two systems can also be reflected by their different values of *N*.

Finally, a comparison between the proposed strategy based on 21 calibration samples and the traditional strategy based on the full experimental design is demonstrated in Figs. 5–8. The spectra of calibration samples with the later strategy were processed by a conventional algorithm: after 15-point smoothing, their second-derivatives were used as variables directly to build a PLS calibration model without any other data processing. The performance of the traditional method was evaluated with the same prediction set in terms of RMSEP, determination coefficient (R^2) and relative error (RE) as the proposed strategy.

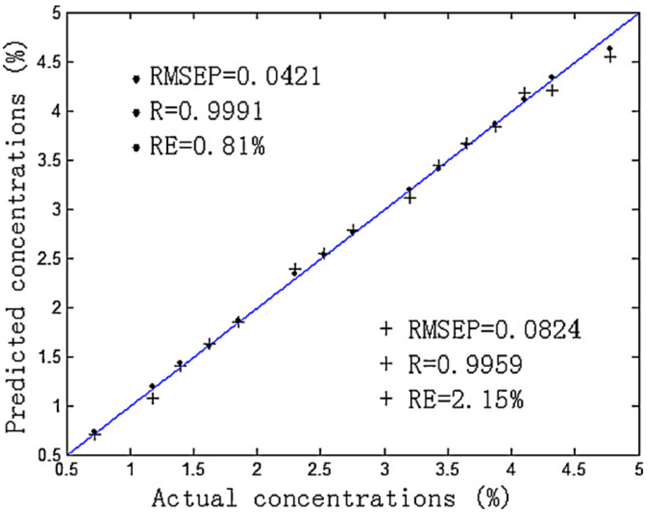

Fig. 6. Predicted acetone concentrations in aniline–acetone carbon tetrachloride system with the proposed strategy based on 21 calibration samples (+) and the traditional method (·).

These figures indicate that in carbon tetrachloride system, predictive ability of two methods were roughly the same, whereas in the aqueous system solution, the proposed strategy was clearly better. This was probably because the strong solvent effect of water made the system more nonlinear and needed more NIR information to correct the nonlinearity. However, the fact that there was even less NIR information available in water solution than in carbon tetrachloride required more concentration levels to deal with this case. Therefore, the full experimental design (10 concentration levels) was more incapable of coping with this problem than the proposed strategy (21 concentration levels).

In order to confirm the discussion, our strategy based on 41 calibration samples were also implemented, and results are also shown in Figs. 7 and 8. From them one could know that predictive ability has obviously been increased and enough for most cases of quantitative analysis. Furthermore, Figs. 7 and 8 show that the method now proposed is also obviously better than our former method [5] based on random experimental design and DWT in aqueous system

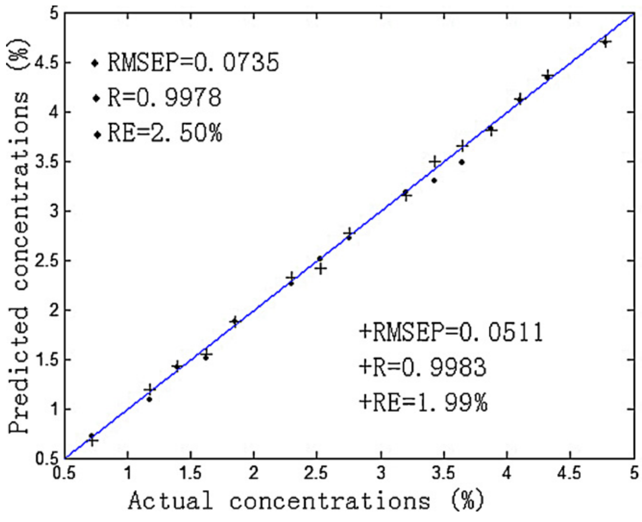

Fig. 5. Predicted aniline concentrations in aniline–acetone carbon tetrachloride system with the proposed strategy based on 21 calibration samples (+) and the traditional method (·).

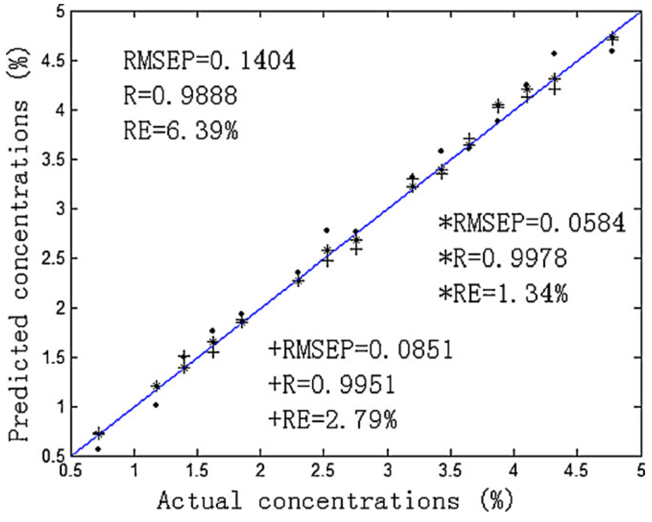

Fig. 7. Predicted aniline concentrations in aniline–acetone aqueous system with the traditional method (·), the proposed strategy based on 21 calibration samples (+) and the proposed strategy based on 41 calibration samples (*).

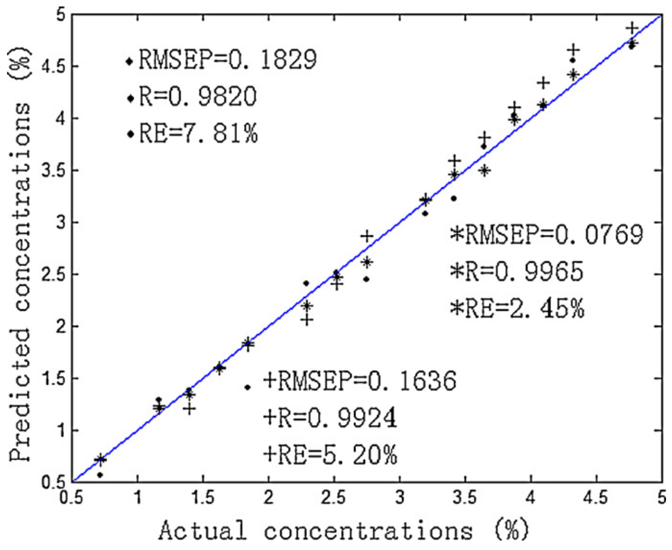

Fig. 8. Predicted acetone concentrations in aniline–acetone aqueous system with the traditional method (·), the proposed strategy based on 21 calibration samples (+) and the proposed strategy based on 41 calibration samples (*).

when the size of calibration set is the same (e.g., both had 41 calibration samples), because the new one has more qualified variables for multivariate calibration model construction even choosing a stricter criterion for variable selection (in our former work, the minimum RMSEP are achieved by 33 variables for aniline and 29 for acetone in tetrachloride system, while 20 for aniline and 18 for acetone in aqueous system). This is probably resulted from two factors: (1) WPT can extract and separate spectral features of various components more effectively than DWT; (2) in the least experimental design, a variables largely related to one component is more likely irrelevant to other components than in the random experimental design. As a result, the innovative one can predict the concentrations of new samples more accurately: the RMSEP of aniline and acetone through the former method are 0.0986 and 0.1250, respectively, while with the new method they are 0.0584 and 0.0769, respectively.

5. Conclusion

The paper shows that it is possible for the proposed strategy to accurately predict concentrations of each component in a multi-component system with a small-scale calibration set. In the proposed strategy, the calibration set should be prepared according to the least correlation design at first, and then their NIR spectra are decomposed with WPT according to the best decomposition tree. The *r*-test is performed to select suitable wavelet coefficients as variables for constructing PLS models. The criterion for variable selection could be adjusted through changing the significance level of the *r*-test to optimize the multivariate calibration model. In general, for the system with more abundant NIR information, a stricter criterion could be applied and more precise predictions could be obtained, while in the system with scarce NIR information like aqueous system, the criterion should be looser in order to let more variables build multivariate calibration model. Although the looser criterion may impair the predictive precision, our proposed strategy can still predict the concentration satisfactorily in most cases with fewer calibration samples as compared with traditional one based on full experimental design or improved one based on DWT and random experimental design.

In NIR quantitative analysis nearly all practical samples are multi-component systems, and in most cases, more than one component is required for quantitative prediction at the same time. Consequently, the strategy suggested here may make the analytical process more economical, rapid and convenient. Although three examples provided in the paper are two-component and homogeneous systems, in fact, our strategy may be carried our even more efficiently for those systems containing more than two components or heterogeneous, since in those cases more calibration samples or calibration samples more difficultly prepared are necessary if they are treated with other usual chemometrics methods.

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