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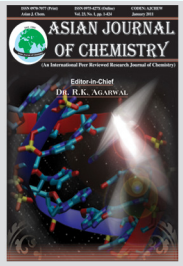

Simultaneous Spectrophotometric Determination of Triphenylmethane Dyes in Complex Samples Using Synthetic Accommodation of Unknown Interferents During Partial Least Square Regression

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The detection of unmodeled interferences in new samples, a convenient way to extend the model is to re-calibrate it using new incoming samples. However, it may be difficult and cost effecting to collect a large number of new samples. If the spectral shape of the unmodeled spectral component can be obtained and mathematically added in variable amounts to the original calibration spectra, then a new synthetic multivariate calibration model can be generated from the augmented data to accommodate the presence of the unmodeled source of spectral variation. This method is demonstrated for simultaneous determination of new fuchsine, crystal violet and malachite green in the presence of unmodeled interferences which are present in the unknown samples. The synthetic accommodation of unknown interferents during partial least square regression eliminates the need for expensive regeneration of new calibration samples and collection of their spectra. The results indicate the successful applicability of the proposed method in complex samples.

Key Words: Unmodeled interference, Multivariate calibration, Synthetic models, New fuchsine, Crystal violet, Malachite green.

INTRODUCTION

Analytical chemistry involves samples that are far from simple, containing numerous components to be analyzed simultaneously or a few target analytes in the presence of many chemical interfering species which affect the instrument response. The term interferent, according to the IUPAC[1] is a systematic error in the measure of a signal caused by the presence of concomitants in a sample.

The development of selective analytical methods has for long been one of the chief goals of analytical chemists. Unfortunately, few available reagents and techniques are satisfactorily selective. It is thus hardly surprising that much endeavor from analytical chemists has focused on research for interference detections and their eliminations. Interference problems were originally dealt with by masking, precipitation and extraction procedures, the last two being not only rather laborious, but also markedly prone to errors arising from intensive manipulation of samples. The advent and subsequent development of chromatographic techniques raised great expectations in this field. However, they proved to be much less efficient than originally expected. Late breakthroughs in computer science have fostered the development of mathematical procedures for offsetting the lack of selectivity of most existing analytical methods[2,3].

The acceptance and implementation of multivariate calibration techniques has grown rapidly in the last decade[4,5] especially in the field of spectroscopy. The recent popularity of multivariate methods can be attributed to the advantages inheriting in first order calibration: (a) complete selectivity of sensors is not required[6], (b) multicomponent analyses can be performed simultaneously[7] and (c) combination of little or no sample preparation with high speed quantitative analysis[8].

One of the most serious problems with multivariate calibration methods is the lack of possibility to handle interferents which are not present during calibration[9]. On the other hand it is necessary to obtain good "representative" calibration set, *i.e.*, calibration set must contain all the relevant variations in the measured signals, which can be expected in the future samples to be predicted[10]. Partial least squares (PLS) and principal component regression (PCR) are found now a day to be the most powerful, generally useful and standard techniques of the linear multivariate modeling methods[9]. An interesting characteristic of these inverse multivariate over classical multivariate regression methods is that calibration can be performed by ignoring the concentrations of all other absorber components except the analyte of interest[11].

Fortunately, in applying projection-based calibration methods such as PCR and PLS, outlier (interferents) detection procedures can be easily implemented[12].

Whatever the calibration model, it is important to check that the calibration samples are representative of the unknown samples to be predicted, *i.e.*, the prediction samples are compa-

rable to the calibration ones. If a prediction samples is different from the calibration samples, it can be considered to be an "outlier in prediction" (or a "prediction outlier")[10].

The detection of an unmodeled source of variance within new samples, the usual remedy is to identify the interfering component followed by updating the multivariate model with additional calibration samples, which contain the new chemical interferents[13,14]. These new samples are then added to the old calibration set and the calibration procedure is repeated using this extended set[8]. Regeneration of the samples, spectra and model can be extremely time consuming and expensive. An alternative for dealing with the problem of spectral interferents using a mathematical method to correct for the effect of interferent has been the subject of most researchers[15-18]. Halland[9] described a synthetic method for accommodating unmodeled interferences (if the spectral shape of the unmodeled interferent can be obtained by independent means) using PLS calibration without the necessity of expensive regeneration of the calibration samples and collection of their spectra. In this paper, we propose Halland method[9] for resolving prediction mixtures containing analytes and one or more than one uncalibrated interfering components.

Triphenylmethane (TPM) dyes are an important class of commercial dyes that have potential applications in the textile industry as sensitizers for photoconductivity and in medicine as antibacterial and sterilization agents during blood transfusions[19-24]. The TPM dyes are characterized by their intense colours, which include vivid reds, blues, greens and violets. Due to the wide range of applications, the TPM dyes are often found in wastewaters and some of these dyes have been found to be carcinogenic and genotoxic[25,26].

Among the TPM dyes, crystal violet (CV) and malachite green (MG) have been widely used [usually together and/or with other TPM dyes such as new fuchsine (NF)] around the world in textile industry to colour silk, wool, leather, cotton and paper and as fungicide, parasiticide and antiseptic in the aquaculture and fish farming industry[27,28].

Malachite green is suspected to act as a tumor promoter and studies have shown that it is highly toxic to fresh water fish[29-31]. Crystal violet is also carcinogenic and is not approved for use in aquaculture[27]. About 20 % of the dyestuff produced in the world is discharged into streams without any pretreatment[32]. Thus, it has been banned to use malachite green and crystal violet in aquaculture in many countries[33]. However, due to their low cost and high effectiveness, these harmful dyes are still used and will probably continue to be used in the aquaculture in some parts of the world. Thus, development of sensitive and reliable method is necessary for the determination of malachite green and crystal violet in environmental samples such as wastewaters.

Several methods have been proposed for this purpose, such as liquid chromatography-tandem mass spectrometry[34], liquid chromatography-visible spectrophotometry[35], capillary electrophoresis-Raman spectroscopy[36] and magnetic solid phase extraction-spectrometry[37]. These methods developed in literature often require complicated pretreatment procedures, which prompt us to develop some alternative methods with simple pretreatments for the determination of malachite green and crystal violet when they coexist with some chromophorous interferents in gray mixture.

To the best of our knowledge, simultaneous analysis of malachite green, crystal violet and new fuchsine have not yet been explored. In present work, we introduce a simple and low cost procedure for simultaneous spectrophotometric determination of these three triphenylmethane dyes in complex samples by the aid of synthetic accommodation of unknown interferents during partial least square regression. The suggested method has been successfully used for the analysis of synthetic and simulated textile waste water samples with satisfactory results.

EXPERIMENTAL

All chemicals used in the experiments were of analytical grade and used without further purification. All solutions were prepared with doubly distilled water. Stock solutions of 100 mg L^{-1} of malachite green (Merck), crystal violet (Merck) and new fuchsine (Merck) were prepared in 0.1 mol L^{-1} acetic-acetate buffer of pH 4 as the solvent and were stored in plastics amber bottles at 5 ºC and protected from light.

Working solutions were prepared by appropriate dilution of the stock solutions.

Acetic-acetate buffer of pH 4 was prepared by adding 1 M sodium hydroxide (Merck) to acetic acid (1 M), a Metrohm 620 pH meter was used to adjust the pH to 4. A solution of potassium chloride (2.5 mol L^{-1}) was prepared by dissolving 46.5938 g KCl (Merck) in water and diluting to 250 mL in a volumetric flask.

Twenty five calibration samples of mixture of the three analytes were prepared according to a 5-level Taguchi orthogonal array design in the concentration range of 1-3 mg mL^{-1} for crystal violet, 1-3 mg mL^{-1} for malachite green and 1-5 mg mL-1 for new fuchsine.

Additionally, 20 prediction mixture samples (from the interested analytes and sunset yellow, tartarazine and amaranth as interferents in different concentrations) were built to test the proposed method. The analytes concentrations were within their corresponding calibration ranges and following random design.

Simulated textile wastewater was prepared from a mixture of dyestuffs (sunset yellow, amaranth, tartarazine, new fuchsine, malachite green and crystal violet) and sodium acetate (1 M) in farming water. 1 mL of this sample was diluted to 50 mL with water.

The impurities of the waste waters were first removed by a filter film and they were immediately used for experiments.

All experiments were done in 0.125 M of KCl to maintain the ionic strength at a constant level and in 0.1 M acetic-acetate buffer of pH 4 (in this pH the analytes have more stability, at higher pH values they become colourless). About 2 mL of solution of calibration or prediction sample was added into the 1 cm path length fused silica cell. UV-visible absorbance spectrum of the solution was recorded against a blank solution and stored in the range of 350-700 nm by an Agilent 8453 photodiode-array spectrophotometer. The spectrophotometer was interfaced to a personal computer, furnished with the G1115A software.

The ParLes package[38] for implementation of PLS regression (PLSR) algorithm was used. The mathematical program MATLAB 7.6.0 (R2088a) (Math Works, Cochituate Place, MA) was used for data processing.

Theoritical background: For all of multivariate calibration model, a calibration set should be constructed having m calibration samples (m is the number of calibration samples and is depending to the number of analytes to be determined) for the analyt with concentrations equally distributed in the linear range[39]. Given the calibration model, while the concentration of an unknown sample that falls within the calibration space, can be unbiasedly predicted.

If sources of spectral variation that are not included in the original model are contained in the unknown sample spectra, then significant prediction errors can occur. So, the analyst could be warned before giving an erroneous result if it be checked that the calibrations samples are representative of the unknown samples.

To detect and mark the new sample, as prediction outlier[10,40-41], that contain interferents which is not present during the calibration, a briefly presentation is warranted based on "the root mean square error in spectral residual" (RMSSR)[2].

The RMSSR value is calculated by projecting the x-data of the prediction sample, x_u, on the optimal factor (principal component, PC) space defined in calibration using PCA and computing $e_{x,u}$ and RMSSR:

$$RMSSR = \frac{\| e_{xmu} \|}{j^{1/2}} = \frac{\| x_u - ppx_u \|}{j^{1/2}} \quad (1)$$

where $\| \cdot \|$ indicates the Euclidean norm and j is the number of channels (*e.g.*, wavelengths) that data are monitored.

Comparison with the RMSSR values of the calibration samples can help to identify new samples containing an interferent. To obtain a cutoff value "$RMSSR_{limit}$" above which the prediction sample is considered as an outlier, sort the RMSSR values of the calibration data in increasing order; the 95 % quantile of these ordered data can be used as the cut-off value. The reason why $RMSSR_{max}$ is not directly used as a cutoff for indicating extrapolation is that for PCR and PLS models, some of the spectral noise characteristics of the calibration spectra are always incorporated into the spectral variables[40]. If PLS is used to construct the final calibration model, the new spectra are projected in the calibration factor-space instead of the PC-space.

If the source of the unmodeled interference can be determined, then the spectral shape of the interferent can be obtained by a variety of experimental methods.

Once the spectrum of any unmodeled interferent has been obtained, it can be synthetically added to the original calibration spectra in a random or designed fashion over the range of variation that might be expected in future unknown samples. These synthetic spectra are calculated by:

$$A_s = A + R\hat{K}_u^T \quad (2)$$

where A_s = m × j matrix of new synthetic calibration spectra, A = matrix of measured calibration spectra, R = m × n matrix of random numbers (n = number of the unmodeled interferents) and $\hat{K}_u$ represents the j × n matrix of the estimated pure-component spectrum of the unmodeled component obtained from classical least square (CLS). Best prediction results are expected if R spans the range of variations that might be found in the unknown samples.

The original multivariate calibration method (PLS in this case) is then applied to A_s to obtain a new synthetic calibration model that includes the major effects of the interferent on the calibration spectra. Thus, the new multivariate calibration model modified by the appropriate shape of the interferent should be able to predict the analytes of interest in the presence of the previously unmodeled contaminant in the unknown samples.

The above procedures[9] are similar to a dry-lab method since the synthetic generation of sample spectra does not require regeneration of the entire set of calibration samples in the laboratory. Thus, the effects of any unmodeled component on the sample spectra can be incorporated into the multivariate calibration model with a minimum of new experimental data being collected.

RESULTS AND DISCUSSION

The applicability of the proposed method was confirmed by simultaneous spectrophotometric determination of crystal violet, malachite green and new fuchsine in presence of some uncalibrated interferents *e.g.*, sunset yellow, amaranth and tatrtarazine. As Fig. 1 shows, the absorption spectra of these analytes and the interferents overlapped in the wavelength region of 350-700 nm.

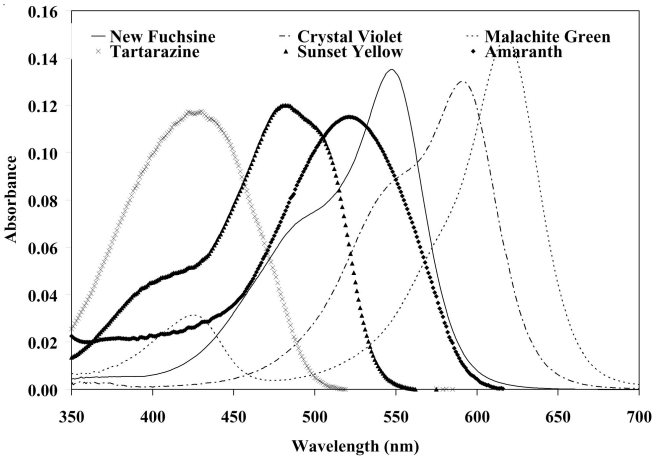


Fig. 1. Normalized spectra of new fuchsine, crystal violet and, malachite green, as the analytes and tartarazine sunset yellow and amaranth, as the unmodeled interferents

The calibration set contains 25 standard solutions (Fig. 2). In Table-1, the compositions of the ternary mixtures that were used in the calibration matrix are summarized. For prediction set (Fig. 3), 20 mixtures were prepared from the analytes (new fuchsine, crystal violet and malachite green) and the interferents (sunset yellow, amaranth and tatrtarazine) (Table-2).

The initial, PLS model was constructed using calibration matrix (A) for ternary mixture of the new fuchsine, malachite green and crystal violet. The optimal model according to the cross validation[42] has three PLS- factor. For testing whether new samples fall within the calibration space, the spectra of calibration and prediction samples projected in the calibration 3 factor-space of PLS. Fig. 4 compares the RMSSR-values for all original calibration and prediction samples *versus* the

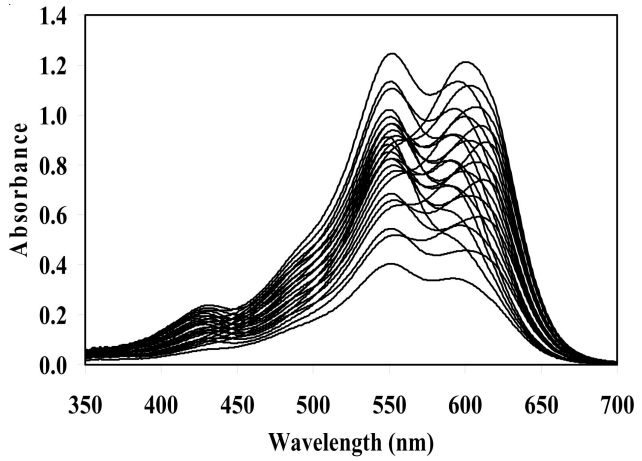


Fig. 2. Spectra of 25 original calibration samples of new fuchsine, malachite green and crystal violet at pH 4

TABLE-1
COMPOSITION OF THE ORIGINAL CALIBRATION SAMPLES

Sample	Concentration (μg mL^{-1})		
	New fuchsine	Malachite green	Crystal violet
1	1.0	1.0	1.0
2	1.0	1.5	2.0
3	1.0	2.0	3.0
4	1.0	2.5	4.0
5	1.0	3.0	5.0
6	1.5	1.0	2.0
7	1.5	1.5	3.0
8	1.5	2.0	4.0
9	1.5	2.5	5.0
10	1.5	3.0	1.0
11	2.0	1.0	3.0
12	2.0	1.5	4.0
13	2.0	2.0	5.0
14	2.0	2.5	1.0
15	2.0	3.0	2.0
16	2.5	1.0	4.0
17	2.5	1.5	5.0
18	2.5	2.0	1.0
19	2.5	2.5	2.0
20	2.5	3.0	3.0
21	3.0	1.0	5.0
22	3.0	1.5	1.0
23	3.0	2.0	2.0
24	3.0	2.5	3.0
25	3.0	3.0	4.0

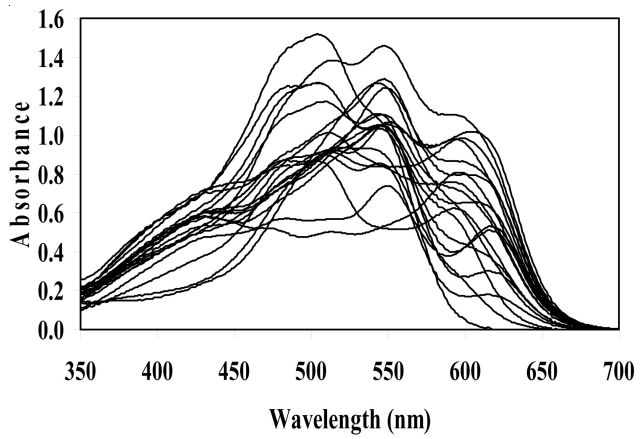


Fig. 3. Spectra of 20 prediction samples that are the mixtures of new fuchsine, malachite green , crystal violet, sunset yellow, amaranth and tatarazine at pH 4

TABLE-2
COMPOSITION OF THE PREDICTION SAMPLES

Sample	Analytes			Interferents		
	New fuchsine	Malachite green	Crystal violet	Sunset yellow	Amaranth	Tartarazine
1	2.4	2.0	2.2	11	7	18
2	2.7	0.0	1.9	0	17	40
3	0.0	2.5	3.8	8	12	16
4	2.7	2.8	4.0	10	11	0
5	1.9	2.0	1.0	0	18	0
6	2.4	2.3	0.0	14	6	30
7	0.0	2.2	2.2	8	15	13
8	1.6	1.2	3.2	2	15	33
9	2.9	2.0	3.5	2	8	34
10	2.9	1.5	3.8	4	11	37
11	0.0	2.1	1.4	13	5	23
12	2.9	0.0	3.4	4	0	24
13	2.9	0.0	3.3	12	11	11
14	1.5	1.0	0.0	4	16	0
15	2.4	0.0	0.0	14	19	20
16	0.0	2.5	2.5	5	3	41
17	1.3	2.1	4.8	3	11	27
18	2.7	1.0	1.7	4	9	50
19	2.4	2.9	2.9	9	0	0
20	2.9	0.0	1.1	7	7	22

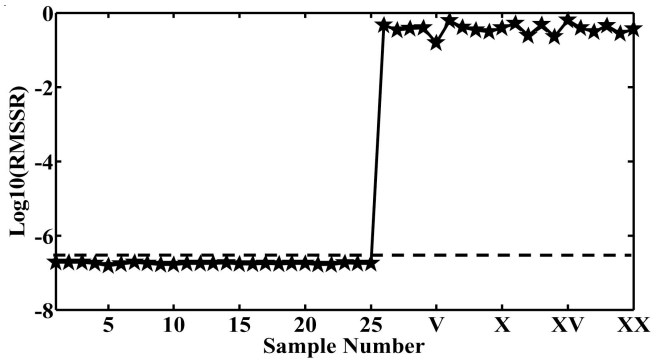


Fig. 4. Log. of RMSSR-values for original calibration samples and prediction samples. $RMSSR_{limit}$ indicated by dashed horizontal line (- - -). Calibration samples: 1-25; prediction samples: I-XX

$RMSSR_{limit}$. The RMSSR-values and $RMSSR_{limit}$ are plotted on a logarithmic scale for clarity.

The $RMSSR_{limit}$ was chosen as the 95 % quantile value of the calibration set by the MATLAB quantile function. As can be seen and we expect RMSSR for all of the prediction samples far exceed the $RMSSR_{limit}$, indicating the occurrence of unmodeled component(s) within them.

It is assumed that the sources of the unmodeled interferences are known, so, we could obtain the spectral shape of the interferents by experimental methods (recording the UV/vis spectra of the sunset yellow, amaranth and tartarazine by the spectrophotometer at pH 4).

Classical least square method was applied to obtain the unit pure spectrum of the interferents. Classical least square calibrations generate the linear least-squares estimate of the spectrum of the Beer' s law pure spectral components as they exist in the average environment of the calibration samples[43].

The unit spectra of the interferents components were constructed as a matrix, $\hat{K}_u$,. Then, $\hat{K}_u^T$ was multiplied by a matrix (R) of uniformly distributed random numbers from the range of 0-60, over the range of variation of the interferents in

unknown samples. The size of R was 25 × 3 (the number of calibration samples is 25 and 3 is due to the number of the unmodeled interferents). Resulting of $R \times \hat{K}_u^T$ was synthetically added to the original calibration spectra to generate the updated calibration matrix, A_s (eqn. 2).

Partial least squares model was constructed with updated calibration matrix, A_s. Fig. 5 compares the RMSSR-values for the prediction samples *versus* the $RMSSR_{limit}$ for the updated calibration model. The RMSSR-values for all of the prediction samples fall within the $RMSSR_{limit}$, indicating that these samples now lie inside the defined multivariate model space.

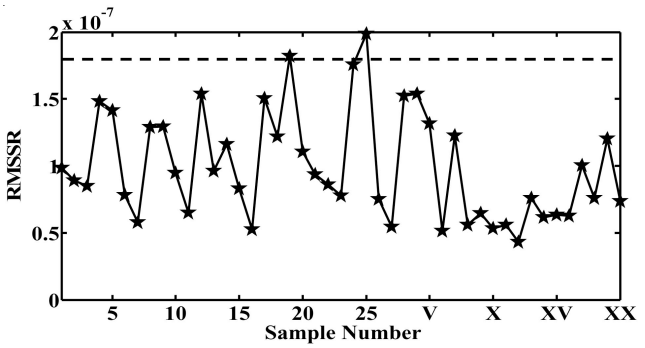
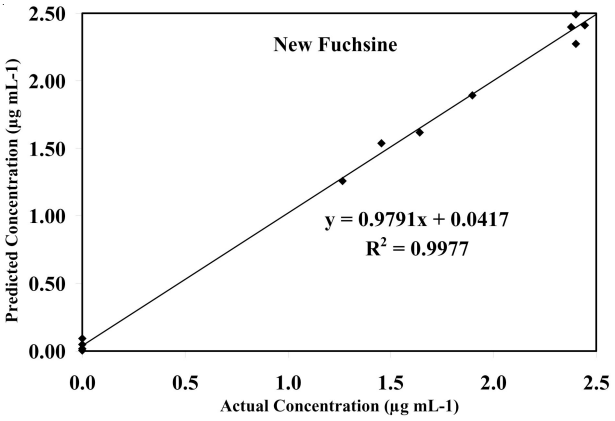


Fig. 5. RMSSR-values for the updated calibration samples and prediction samples. $RMSSR_{limit}$ indicated by dashed horizontal line (- - -). Calibration samples: 1-25; prediction samples: I-XX

Finally, the corresponding A_s was applied to constructed the new PLS1 models for determination of new fuchsine, malachite green and crystal violet in the prediction samples. The optimal updated models according to the cross validation have 6 PLS-factor for new fuchsine, malachite green and crystal violet. The plots of the predicted concentration versus actual values are shown in Fig. 6 for new fuchsine, crystal violet and malachite green (line equations and R^2 values are also shown).

Statistical parameters: The relative standard errors (RSE) and recovery values parametrs were selected to assess accuracy and prediction ability of the proposed method for simultaneous determination of new fuchsine, crystal violet and malachite green in presence of unmodeled interfernts.

The relative standard error (RSE) of the prediction concentration was calculated as the prediction error of a single component in the mixture:



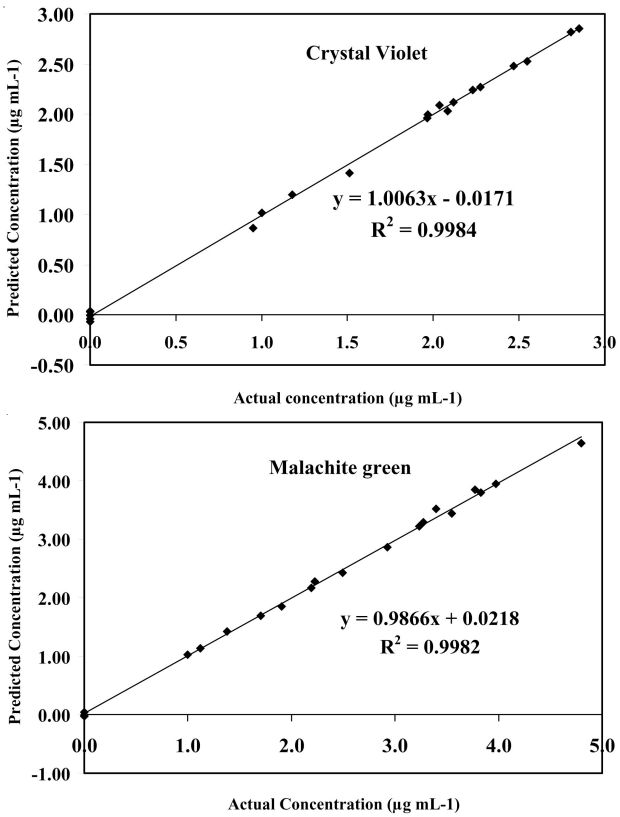


Fig. 6. Predicted concentration *versus* actual concentration obtained for new fuchsine, crystal violet and malachite green in the prediction set

$$\text{Relative standard errors } (\%) = 100\sqrt{\frac{\sum_{j=1}^{N}(\hat{C}_j - C_j)^2}{\sum_{j=1}^{N}(C_j)^2}} \quad (3)$$

where N = number of samples, C_j = concentration of the component in the jth mixture and is $\hat{C}_j$ = estimated concentration.

The recovery of the prediction concentration was calculated as:

$$\text{Recovery } (\%) = 100 \times \frac{\left(\sum_{j=1}^{N}\left(\frac{\hat{C}_j}{C_j}\right)\right)}{N} \quad (4)$$

The obtained results (Table-3) show that there are good agreements between actual and predicted concentrations of the analytes which confirm the accuracy of the applied method.

TABLE-3
STATISTICAL PARAMETERS OF THE PROPOSED METHOD FOR THE PREDICTION SET

Parameters	Analytes		
	New fuchsine	Malachite green	Crystal violet
Relative standard errors (%)	2.57	2.21	2.29
Recovery (%)	98.90	99.30	101.00

Environmental samples: For evaluating the ability of the proposed method to analyze the real samples, with complex matrices, the proposed method was successfully applied to

TABLE-4
DETERMINATION OF NF, CV AND MG IN SIMULATED TEXTILE WASTE WATER BY THE PROPOSED METHOD

Sample	Added (μg mL^{-1}) (standard addition)			Found* (μg mL^{-1}) (total)			Recovery (%)**			RSD***		
	New funchins	Crystal violet	Malachite green	New funchins	Crystal violet	Malachite green	New funchins	Crystal violet	Malachite green	New funchins	Crystal violet	Malachite green
1	–	–	–	2.03	0.97	1.64	–	–	–	1.40	2.02	1.28
2	1.00	–	3.75	3.14	1.01	5.37	105.6	104.1	98.9	0.88	1.16	0.12
3	2.20	2.50	–	4.29	3.54	1.77	103.0	107.1	107.8	1.18	1.41	2.90
4	3.00	1.25	1.80	5.13	2.37	3.41	105.0	115.4	98.2	1.94	1.09	1.62

*Mean of three replicate measurement. **Recovery (%) = 100 × (C_{found} – C_{added})/$C_{orginal}$. ***Relative standard deviation (n = 3).

the simultaneous determination of new fuchsine, malachite green and crystal violet in simulated textile waste water.

The analytical results obtained by the proposed method are summarized in Table-4, in which the recoveries obtained by standard additions to sample are listed and compared with the results obtained before and after of their addition to the sample.

The good agreement between the obtained results and known values indicates the successful applicability of the proposed method in complex samples.

Conclusion

This study has shown that when unmodeled spectral interferents are present in the unknown sample spectra, then full regeneration of the calibration samples is not required[9] if the spectral shape of the unmodeled interferent can be obtained by independent means. This synthetic procedure to correct quantitative multivariate spectral models can greatly reduce the time, effort and expense of regenerating the entire sample set and spectral data. The reliability of the predictions can be assessed since the spectral outlier detection methods are still available with the synthetic model. The method should work for those cases where the effect of the interferent(s) is(are) linear over the concentration range of the interferent in the unknown samples.

We demonstrated the application of the method in simultaneous determination of new fuchsine, crystal violet and malachite green with unmodeled interfernts. The good agreement between the obtained results and known values indicates the successful applicability of the proposed method in complex samples.

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