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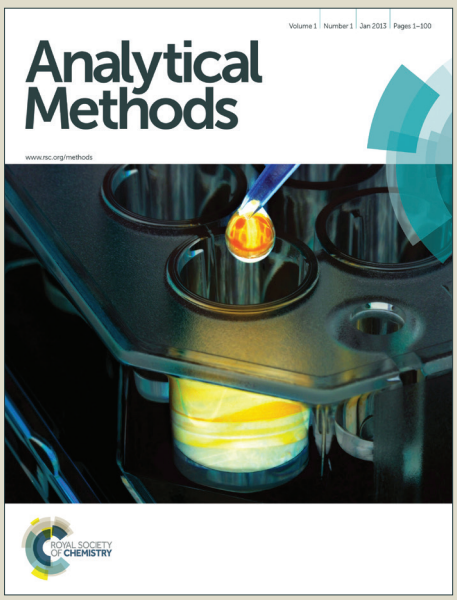

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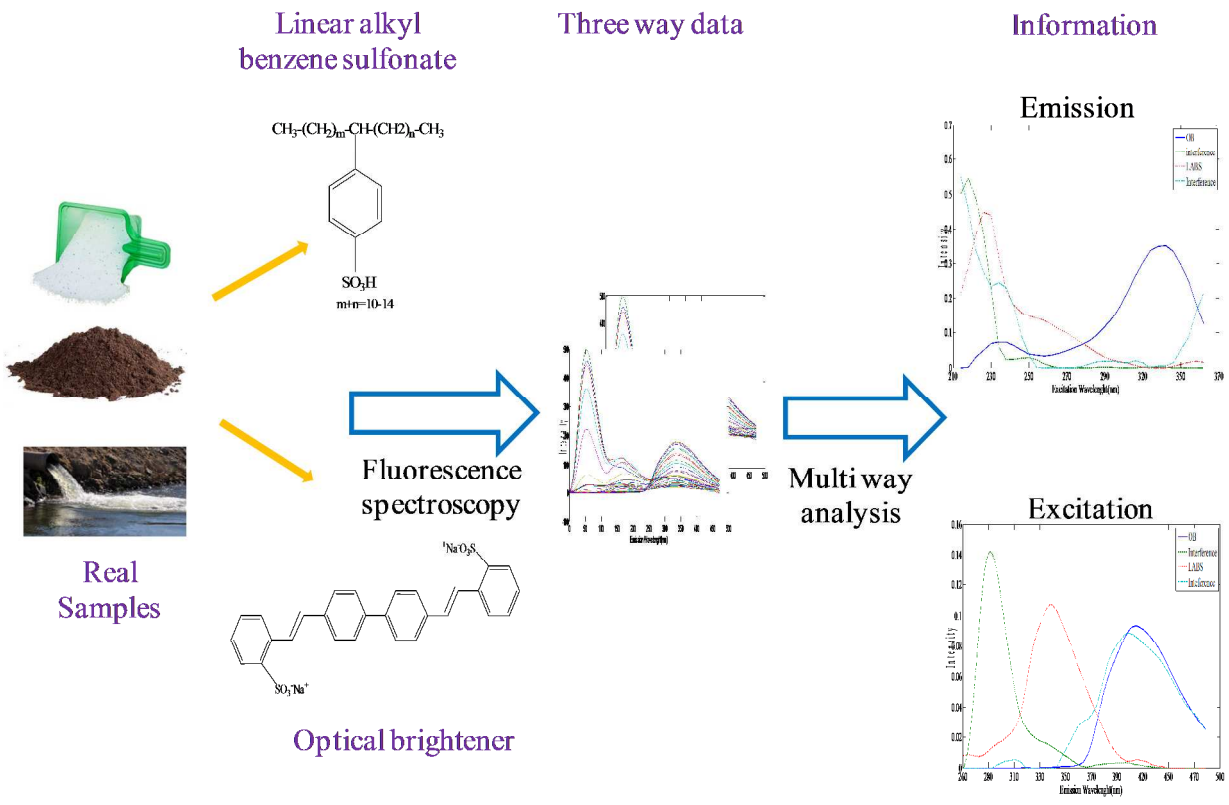

The employed second-order calibration is one of the non separative methods for simultaneous determination of LABS and OB in a complex matrix.

Model-based three way chemometric methods for quantitative analysis of linear alkyl benzene sulfonate and optical brightener in real samples using excitation–emission fluorescence data

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Abstract

A sensitive and rapid spectrofluorimetric method has been proposed for the quantitative analysis of linear alkyl benzene sulfonate (LABS) and optical brightener (OB) in the presence of unknown interferences with intense spectral overlapping in laundry powders and environmental samples. The method is based on second order multivariate calibration applying three way chemometric methods. Due to unique solutions of the three way data analysis methods and analogy between the structure of LABS and OB, it is apparent that these methods can resolve overlapping signal into pure spectra and relative concentration profiles. Satisfactory recoveries for the spiked laundry powders for LABS (92.8 %-109.3 %) and OB (97.1% -105.2%) indicate the high accuracies of the proposed calibration methods for the assessment of LABS and OB in laundry powders. In the case of environmental samples, recoveries of 98.0-109.3% for LABS and 94.0-107.7% for OB show the present method successfully faces this complex challenge without the necessity of applying separation steps.

Keywords

Spectrofluorimetric analysis, Linear alkyl benzene sulfonate, Optical brightener, Laundry powder, Environmental samples, Second order calibration methods

1. Introduction

Laundry powders are type of detergents that refer to the mixture of chemical components, including linear alkyl benzene sulfonate (LABS), optical brightener (OB) and etc. LABS is used as an anionic surfactant in many laundry powders and cleaners in the form of the sodium salt. It was introduced in the world market in 1964 as a biodegradable replacement for branched alkyl benzene sulfonates when the low rate of biodegradation of branched-chain alkylbenzene sulfonates (BAS) was recognized. It contains an aromatic ring, sulfonated at the para position and attached to a linear alkyl chain with 10 to 13 carbon atoms at any position except the terminal carbons. [1-4] LABS does not cause irritation to the skin or eyes at low concentrations levels (0.5-2.5%), but it causes moderately irritation at 5%, and more irritation at higher concentrations levels (about 50%).[5,6] Because of the extensive applications of anionic surfactants, a considerable amount of LABS is released into the environment, as wastewater, which produces intensive pollution of water reservoirs. These surfactants and especially the products of their degradation may remain for long periods of time and can be caused the reduction of the available oxygen for aquatic organisms by formation of foams in rivers and surface waters. LABS is harmful to human beings, fish and vegetation, and it can act synergistically with other toxic chemical presents in soil and water, after entering into soils and waters. Therefore, a simple and applicable method for the LABS determination in water could be helped to determine suitability of the water for drinking purpose.[7]

There are different acceptable methodologies, which are used for the assessment of LABS in various real samples. These methods are classified as separative and non-separative techniques. Chromatographic methods include high performance liquid chromatography (HPLC) with UV and fluorescence detection and gas chromatography (GC) serve as separative ones while two

phase titration using various dyes such as Methylene Blue, Rhodamine 6G, spectrophotometric and electrochemical methods fall in the second category. HPLC methods are expensive, time consuming and only can be applied to relatively clean aqueous samples that have quite high contents of LABS. The gas chromatography procedures require the conversion of LABS into volatile derivatives before the analysis, because the anionic surfactants have low volatility. Spectrophotometric methods suffer from interferences due to the presence of other substances, such as organic sulfonates, carboxylates, and phenols have the maximum wavelength similar to LABS.[8-10] Two phase titration is the standard method for LABS determination but involve toxic chemicals. For example, methylene blue active substance (MBAS) method has been widely applied for measuring sulfonate in wastewater. In this method, toxic chloroform as extracting solvent has been used. This method is time consuming and suffers from interferences due to the presence of phenols and inorganic thiocyanates, cyanates, nitrates and chlorides.[7]

CBS-X as an optical brightener is bis-cinnamene monobiphenyl type optical fluorescence brightener. It is the best fluorescence brightener for detergent use and converts UV light wavelengths into visible light, which makes laundered clothes appear whiter (although does not actually affect the cleanliness of the clothing). It dissolves in water and has good whitening effect under the room temperature. Residues of these chemicals are left on our clothes, and they can cause allergic reactions when absorbed by skin. Optical brighteners are not biodegradable, so when they enter into the water system, they pose a potential hazard to aquatic life. This pollution remains in waste water for long periods of time, negatively affecting water quality and animal and plant life. Optical brighteners have caused mutations in bacteria and fish and also in high concentrations, they may cause cancer.[11,12] Most HPLC methods with a fluorescence detector are used for determination of OB in different samples, but they need expensive solvent and

instrumentation.[13,15] If there is another type of optical brightener, these methods do not give individual concentration of them and measure only total concentrations. A second problem is that natural waste waters and soil samples usually contain a number of organic species, often at relatively high concentrations, which can interfere with the optical brightener's quantification. [16]

One of the most important challenges in analytical chemistry is the analysis of a complex matrix with unknown components. Since the introduction of chemometric methods in analytical chemistry, these methods allow the analysis and quantitation of analytes in such complex matrices without any prior knowledge about their chemical substances. The second or higher order data analysis methods can be used for the quantification of analytes in the presence of unknown and uncalibrated interferences. The latter feature universally recognized as the second order advantages.[17] The second order methods need a three-way array of data that is obtained by staking the data matrices of different samples under each other.[18,19] In fluorescence spectroscopy, the emission spectra are typically studied. A more informative way to analyze the data, is exciting the sample at different excitation wavelengths for obtaining the emission spectra. The obtained data can be seen as an excitation–emission matrix (EEM). Each EEM is a matrix, and by combining EEMs from several samples, a three-way array is obtained (sample × emission × excitation).[20] If the data are approximately trilinear, multi-way models, such as parallel factor analysis (PARAFAC), alternating trilinear decomposition (ATLD), alternating penalty trilinear decomposition (APTLD) and self-weighted alternating trilinear decomposition (SWATLD) can predict analyte concentrations in new samples.

This study shows how multivariate data analyses methods can be applied to the study of EEMs for the simultaneous determination of LABS and OB with spectral overlap in the presence of uncalibrated and unknown interferences in laundry powders and environmental samples.

In some previous studies, partial least-squares (PLS) method was used for simultaneous determination of family of these components. [21-24] Actual environmental samples contain different material such as colored or chromophoric dissolved organic matter (CDOM), organic acid such as fulvic acids and humic acid, humin, chlorophenols and other kind of surfactant or optical brighteners, which have been intense spectral overlapping with measuring analyte. In practice, identifying all components either is too costly or impossible. Quantitative analysis of analyte in a complex mixture without physical separation and using few standard samples is dream of an analytical chemist but a drawback of PLS and related methods are that a large number of calibration and test samples are necessary, and also all possible analytes and interferences have to be included in the calibration set at suitable concentration levels to obtain a robust regression model. Spectrum overlapping was resolved by these methods, but unfortunately, they don't exhibit the second-order advantage**,** i.e. analysis in the present of unknown interferences. Therefore, all the components in the complex samples must be known. This is the main advantage of our propose methods compared to the previous studies in the environmental analysis.

To the best of our knowledge, this is the first application of multi-way methods in the multi-dimensional analysis of the main components in laundry powders and environmental samples.

2. Theory

2.1. PARAFAC modeling

Parallel factor analysis (PARAFAC) modeling of a three-way array is given by three loading matrices, A, B and C, with elements a_{if}, b_{jf} and c_{kf}, respectively. In excitation-emission matrix, F is the total number of responsive components, a_{if} is the relative concentration of component f in

the *i*th sample, b_{if} is the signal intensities at emission wavelength *j* and c_{kf} is the signal intensities at excitation wavelength k in each dimension for component f. The trilinear model was used to minimize the sum of squares of the residuals, e_{ijk}, in the model. The PARAFAC model can be written as following equation.

$$x_{ijk} = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} + e_{ijk} \quad (1)$$

Where x_{ijk} is the intensity of the ith sample at the jth variable (emission mode) and at the kth variable (excitation mode).[25] The PARAFAC analysis was performed using the N-way toolbox in MATLAB environment provided by Rasmus Bro.[26]

2.2. ATLD modeling

An alternating trilinear decomposition (ATLD) is an improved alternative algorithm for decomposition of three way data arrays. It retains the second-order advantage for quantification of analytes even in the presence of unknown interferences. This algorithm aims at using Moore–Penrose generalized inverse and diagm operation, which can give the advantage of being insensitive to the estimated component number. The calculation is based on slice matrices, which makes its convergence very fast. In this method, the matrices **B** and **C** of orders J×N and K×N, respectively, were initialized using different methods. After initialization of B and C, in the next step, computation of **A(I×N)** was performed from, $\mathbf{X_{i..}}$, **B** and **C** by least-squares regression. Then **B(J×N)** was computed in the same way as a matrix **A**. In the following step, computation of **C(K×N)** was estimated from $\mathbf{X_{..k}}$, **B** and **A**. Stop criteria are relative to an absolute change in a fit of 10^{-6}, and the fitting stopped until a certain stop criterion has been reached.[27,28]

The ATLD analysis performed using the MVC2 toolbox of MATLAB provided by Olivery.[29]

2.3. APTLD modeling

Alternating penalty trilinear decomposition (APTLD) is developed for the decomposition of three-way data arrays in the presence of potentially unknown interferences. This algorithm utilizes the penalty term which minimizes three new least squares-based constrained objective functions. The value of penalty factors p, q and r should be chosen before implementation of the APTLD algorithm. The proposed algorithm can overcome the slow convergence and being insensitive to increasing number of component by choosing a large number of penalty factors. The following procedures show the algorithm of the APTLD modeling.

1. Obtain the accurate number of species.

1. Randomly initialize **B** and **C** by choosing suitable penalty factors **p**, **q** and **r**.

2. Compute **A** from **V**, **B** and **C** using least-squares regression.

3. **B** and **C** were computed in the same way as matrix **A** in step 3.

4. Providing column wise normalization by scaling **B** and **C**.

5. Repeat steps 2–4 until a relative change in a fit is small.[30,31]

The APTLD analysis was done using the MVC2 toolbox in MATLAB environment provided by Olivery.[29]

2.4. SWATLD modeling

Self-weighted alternating trilinear decomposition (SWATLD) is one of the trilinear decomposition algorithms, which derived from ATLD for second-order linear calibration. The performance of SWATLD is very stable. There are different features for SWATLD such as speed up the optimizing procedure to decrease the computation time in each iteration, being insensitive to the excess factors, second order advantage and the unique optimizing scheme. Developed algorithm is based on the following procedure:

1. Estimate the number of chemical components (chemical rank).

2. Loading matrices **B** and **C** were initializing randomly or by other estimation methods.

3. Estimate **A** from **V**, **B** and **C** by least-squares regression.

4. Estimate **B** and **C** in the same way as matrix **A** in step 3.

5. Update **A**, **B** and **C** according to steps 3–4, until a certain stop criterion has been reached.[32,33]

The SWATLD analysis was done using the MVC2 toolbox in MATLAB environment provided by Olivery.[29]

3. Experimental section

3.1 Materials

The entire chemicals which are used in this investigation were prepared from analytical grade chemicals and distilled water. Sodium dihydrogen phosphate, sodium hydroxide and hydrochloric acid were provided from Merck (Germany). LABS and OB were purchased from the Esfahan petrochemical company (Iran) and Ciba-Geigy Company (Switzerland), respectively. Two analyzed commercial laundry powder samples were purchased from the local market. One waste water sample was obtained from a detergent factory. One agricultural soil sample was gathered near zones with profuse industrial activity.

3.2. Preparation of standard and real samples

The pH of buffer solution was set to 7.5 by dissolving 1.000 g of sodium dihydrogen phosphate in distilled water and addition of 0.1 mol L^{-1} sodium hydroxide. Stock solutions of LABS (10000.0 mg L^{-1}) and OB (10000.0 μg L^{-1}) was prepared by dissolving 1.000 g LABS and OB in distilled water. Then the solutions were heated to the temperature of 40 ^{o}C and diluted to final volume of 100.0 mL with phosphate buffer solution. LABS has a sulfonic acid group; therefore, in laundry powder, it is neutralized and converted to sulfonat salt by adding sodium

hydroxide. So in this study, sulfonic acid group was neutralized by addition of 0.1 mol L^{-1} sodium hydroxide solution. Nine LABS and OB binary mixtures were prepared by appropriate dilution of the stock solutions with phosphate buffer, and all measurements were done in the room temperature. In order to investigate the second order advantages, two real laundry powder samples and also two environmental samples were investigated. Three laundry powder samples were prepared by dissolving 1.000 g of them in distilled water and heated to a temperature of 40^{o}C and diluted to volume of 100.0 ml with phosphate buffer solution. 1.000 g of agriculture soil sample was added to 5 mL distilled water and magnetically stirred for 30 min. Then dissolved sample was filtered through filter paper to remove suspended sediments and solid materials. Also, 5 mL of waste water were diluted with 5 mL distilled water. Before optical analysis of analyte, the waste water and soil samples were allowed to warm to a temperature of 40 ^{o}C. 5 mL of waste water sample and 3 mL of filtered soil sample diluted to volume of 100.0 ml with phosphate buffer solution.

3.3. Instrumentation

A Perkin-Elmer LS 50B luminescence spectrophotometer was used for the fluorimetric measurements. The measurement of pH was done with a Metrohm 691 pH-meter using a combined glass electrode.

3.4. Excitation–emission spectrofluorimetric setup

All measurements were done in a 10mm × 10mm quartz cuvette at the room temperature. For each sample, an excitation–emission data matrix was generated by exciting the sample at 5 nm intervals from 200 to 370 nm with the scan rate of 1500 nm/min. The wavelength range of 250–496 nm with 0.5 nm intervals was selected for obtaining the emission spectra. It was found that

the best intensities were obtained if the excitation and emission slit widths were set at 11 nm and 8 nm, respectively.

4. Result and discussion

4.1. Generation of second order trilinear data

The first step in the three way methods is providing second order trilinear data. To generate fluorescence landscapes, excitation wavelengths between 200-370 nm with 5 nm intervals (35 excitation wavelengths) and emission wavelength range between 250-496 nm with 0.5 nm intervals (493 emission wavelengths) were used. All measurements were made on nine mixtures of alkyl benzene sulfonate and optical brightener at known concentrations. The recorded three-dimensional excitation–emission fluorescence data was smoothed with Savitzky-Golay filter.[34]

4.2. Reduction of the original data

Figure 1 shows an EEM landscape for one of the two real laundry powder samples. In a fluorescence landscape, several light scattering effects usually present, which do not confirm the required tri-linearity. The light scattering effects are called Rayleigh (first and second orders are most common) and Raman scattering which both of these scattering effects originate from the solute. The Rayleigh and Raman profiles are not operatively modeled using three way chemometric models; there is no intrinsic information in the excitation or emission profile that can be extracted. Consequently, the model fails to converge when three way algorithms are applied to analysis of a three way data array without removing the scattering. One possibility for reducing the effects of the Rayleigh and Raman scattering on three way modeling, is to subtract blank matrices from each of the sample matrices prior to analysis. While this may be successful for idealized laboratory analyses, for real samples with saturated Rayleigh scattering and Raman-active species, this approach may be insufficient. The most common way to handle this problem

is to set this value to be missing in analysis.[35-37] To minimize the contribution of scattering in the EEM spectra, the EEM of blank water was subtracted from the data, and all values corresponding to the scattering were set to NaN (not-a-number) refers to missing data and then replaced by their corresponding estimates. Using the missing data to replace scattering light in EEMs has been successfully implemented in this study. The obtained result is shown in Figure 1B. For all data set, excitations from 200 to 205 nm and emissions from 250 to 259 are removed in order to reduce the amount of missing value and to remove some of the second order scatter line. The new dimension of the three way array is thus 9×473×33.

4.3. Number of estimated components

One of the vital points in the PARAFAC analysis is the choice of the appropriate number of factors. In prepared or known samples, the choice of the number of factors can be based on the prior knowledge of the system, as well as using the analysis of the residual model. In the case of natural samples that are not well-described, the choice of the number of factors is much more difficult even for experts. There are several sophisticated chemometric tools to provide information to help in this case, such as percentage of explained variance in the principal component analysis (PCA), standard deviation of residuals (SD), three-way cross validation (CV) and mathematical diagnostic tools (e.g. core consistency diagnostic (CORCONDIA)). In some complex matrices, due to the complexity of the problems, none of these methods can guarantee the correct estimation of the component number under all circumstances. In this work, to estimate the number of variation sources, CORCONDIA, standard deviation of residuals and three-way cross validation were used. Obtained values from CORCONDIA fall between zero (maybe negative values) and 100. When core consistency drops from a high value (approximately above 90%) to a lower value (approximately under 50%), it is shown that an

appropriate number of components has been achieved.[38] For this data set the core consistency diagnostic score was more than 63% for the four component models. Models with more components, yielded core consistencies close to zero, that indicates the four component model provided the greatest spectral resolution for laundry powders data set. According to the standard deviation of residuals, the number of component is four because this stabilizes the standard deviation at the noise level, and nothing is gained by increasing it to five. The basic principle of cross validation is to keep parts of the data out from the model progress which used as the test sample, develop an N-PLS or TUCKER models from the new data and predict the test sample by these models, and finally compare the predicted values with the actual ones. The predictive residual sum of squares (PRESS) is then obtained by calculating the squared variances between predicted and observed values, which is an assessment of the predictive power of the tested model. [39] In the case of cross validation, systematically increasing the number of component in the model, the optimal number of component can be found at the minimum PRESS. PRESS patterns show a steep decrease for four components, but very small PRESS increases (stabilizes PRESS) were detected for higher components, and it is minimum for the four components. This quality is even more pronounced for the laundry powders, which consistently suggests four components (Figure S1). Therefore, there are two unknown interferences not include in calibration set besides LABS and OB in laundry powder. The results attained by above procedures established that the total number of components required by three way chemometric methods in the waste water sample is seven (two components present in the calibration set and five unexpected components). The number of responsive components, selected by applying above listed methods for agricultural soil sample is six. This result suggests that the four new unexpected constitutes incorporated as interferences in this sample, which are not present in the

calibration. Results of these models for determining the number of components are shown in Table 1.

4.4. Implementation of three way component analysis on laundry powders fluorescence data

For all three way data arrays analysis, the starting value is based on DTLD/GRAM decomposition. When the following stop criterion reaches a certain threshold ε ($\varepsilon = 10^{-6}$), the optimization processes of PARAFAC, ATLD, SWATLD and APTLD are finished.

$$\left[\frac{SSR^{M} - SSR^{M-1}}{SSR^{M-1}}\right] \leq \varepsilon \qquad (2)$$

SSR is the residual sum of squares, and M is the current iteration number.

To resolve the actual profiles of the components, the data array of 11 mixture samples were analyzed using the PARAFAC, ATLD, SWATLD and APTLD methods. The first nine samples are used as calibration samples and the last two ones are used as unknown samples. The size of the analyzed array was (11×473×33) and the unknown samples were joined to calibration set for achieving the second order advantages. In all cases, a reasonable least squares fit was obtained. The loading plots provided by PARAFAC analysis of the EEM data of sample1 were shown in Figure 2. The comparison of the excitation and emission profiles extracted by the PARAFAC model with the experimental ones shows a satisfactory agreement. For ATLD, SWATLD and the proposed APTLD with $p=q=r=10^{20}$, the results indicate that three algorithms give satisfactory resolutions for excitation and emission spectral profiles for all samples which are very similar to the obtained loadings from PARAFAC algorithm. The linear least squares calibration curves based on the loading matrix corresponding to the sample mode, were provided over the ranges of 1–8 mg L^{-1} and 0.5–5.5 μg L^{-1} for LABS and OB, respectively. Table S1 shows the obtained coefficient of determination (R^2) from different three way chemometric methods. Three way

methods were applied to the set of calibration and real samples providing the quantitative analysis of two species (Table 2). After the number of components was estimated, the obtained array by joining the EEMs of the standard sample, and spiked samples was subjected to decomposition. Comparison of the predicted concentrations and recoveries provided by three algorithms shows a good predictive ability towards the spiked real samples, and confirms the potentiality of the second-order methods for the analysis of these complex samples for the assessment of LABS and OB (Table 3).

$$\text{Recovery factor} = 100\times(C_{recoverd})/\ C_{true} \quad (3)$$

Where $C_{recoverd}$ is the estimated concentration after adding known concentrations of the measured component to real sample and C_{true} the true concentration.[40]

4.5. Development of chemometric methods for analyzing waste water and soil fluorescence data

In this work, PARAFAC was applied to three way data arrays built by joining the nine data matrices for set of calibration samples, with one of the real environmental samples and this was initialized with the best estimated loadings, provided by generalized rank annihilation method. After processing the three way array, Figures 3 and 4 show the prediction results corresponding to the application of PARAFAC for waste water and agricultural soil samples, are in good agreement with pure spectrum of these components. The obtained results for ATLD, SWATLD and the APTLD with $p=q=r=10^{20}$ illustrate that these algorithms give satisfactory resolutions for excitation and emission spectral profiles for these samples which are very similar to the obtained loadings from PARAFAC algorithm. Recovery experiment by spiking the studied analytes carried out (Table 4). Results suggest that the proposed method is appropriate for the determination of the studied components.

4.5. Comparison between four algorithms

In comparing the above-mentioned multivariate calibration models, one should consider the following features: (1) analytical performance, (2) ease and speed of convergence and program progress, and (3) model prediction ability.

The value of recovery factor, iteration number and calculation time needed for each iteration are given in Table S2 using 4 and 5component numbers with DTLD as an initial value, indicate ATLD is the fastest one, while PARAFAC is slowest. The mean iteration number for APTLD is between PARAFAC and ATLD, but it is same as SWATLD. It is also found when the number of component increases, more iteration numbers are required for these algorithms to converge. If four factors are used as an appropriate number of factors (or components), a reasonable model is achieved. Besides, PARAFAC model of five factors is required a long time and more iteration steps to gain a suitable convergence and the extra components mainly fit the noise in the model.

On the contrary, obtained recoveries by ATLD, SWATLD and APTLD didn't change by increasing component number. So these methods are insensitive to the estimated component number, thus avoiding the difficulty of determining a correct component number for the models, which is the initial and important stage in the PARAFAC algorithm. We should be careful in using ATLD in the situation when the signal-to-noise ratio is low and PARAFAC where two chemical species are present with high degree overlapping. These profiles will be ambiguous, and the optimization procedure does not always converge to chemically meaningful results i.e. unique solutions can't be achieved. In this study, the degree of overlapping between the profiles of all components in the data matrix is appropriate and the signal-to-noise ratio is high, so these four algorithms can provide the same reasonable results, when the sufficient number of component is selected. To predict the concentration of the LABS and OB in the two laundry

powders and two environmental samples, initially, these models were adjusted to extracting the pure spectra of these components from the mixed sample, when modeling a data set with appropriate distributed concentration of each fluorophor. All algorithms give reasonable sample concentration profiles, which extracted scores used for prediction of concentration.

We suspected that the DTLD initialization may not give a suitable starting value to fit these models for obtaining unique results. Therefore, we further used best fitting model as the initial estimate. Three replication runs were done to check the stability of the models but using the best fitting model did not show any obvious variation than DTLD values in improving the fit (Table S3). Either best fitting model or DTLD in all samples can give almost identical results in profile matrices for four algorithms. To consume an extended computation time, DTLD is used as an initial value with a correct component number. While a best fitting model needs more iteration setups, DTLD provides the low number of iteration. Also using DTLD as the initial value, the solutions of PARAFAC, SWATLD, APTLD and ATLD give reasonable results.

On the other hand, the performance of APTLD with regard to choice of the penalty factors p, q, r was inspected. Table S4 discloses that choosing very small p, q and r (such as $p=q=r=10^{-6}$ or 10^{-1}) can cause a large number of iteration setups, and increases sensitivity to an additional number of component used in calculations for the finishing results of APTLD, which is similar to the condition of the PARAFAC algorithm. Also, all of the runs of APTLD with very small p, q and r didn't converge to value of satisfactory recovery, while an extra increase in p, q and r (e.g. $p=q=r=10^{8}$) will lead to better performance to give acceptable results and speeds up the convergence of the algorithm and will make APTLD insensitive to an excess number of component. When p, q and r changing from 10^{8} to 10^{20}, no obvious discrepancy of the quality of the value for recovery factor has been observed but in this paper, we choose $p=q=r=10^{20}$ that lead

to converge faster than other penalty factors. The results of APTLD looks like the same as SWATLD for penalty factors set to 10^{20}, because a large value of penalty factors makes APTLD close to SWATLD.

Table S5 shows the influence of stop criteria on the performance of the four algorithms. The obtained recoveries by ATLD, APTLD and SWATLD algorithms for LABS have no observable differences at each stop criterion. When the stop criterion decreases to 10^{-9}, three algorithms converged comparatively very slow. The obtained result indicates that performance of these algorithms is better at 10^{-6} level. It can be seen a low stop criterion (10^{-9}) put heavy computation burden on PARAFAC and converges very slowly within 2050 iterations.

By comparing the obtained results from these data sets, it was found that simultaneous determination of LABS and OB is possible in the presence of interferences.

Table 5 reports the analytical figures of merit of the four calibration models in a real sample. Sensitivity (SEN) was defined as the slope of the calibration line. The precision for each analyte was considered in terms of concentration according to the following equation:

$$\text{Precision}=S_{res}/SEN=SEN^{-1}\sqrt{\frac{\sum_{i=1}^{I}\left(y_i-\hat{y}\right)^2}{I-2}} \quad (4)$$

Where I is the number of calibration samples, y_i is the loading for the given analyte obtained from the three way algorithms and $\hat{y}_i$ is the loading estimated from the calibration line loading, versus analyte concentration.[41]

Limit of detection (LOD) was calculated directly from the calibration plot. LOD was calculated as $3.3\sigma/SEN$, respectively, where σ is the estimation of random error in the y direction and equal to S_{res}.[42]

5. Conclusion

In this study, a rapid, simple and selective method was developed for simultaneous determination of LABS and OB in the presence of unknown interferences in laundry powders and environmental samples. This study is based on three way analysis of the excitation–emission fluorescence data. These methods enabled us to handle the direct interfering effect of complex samples matrix. The obtained results of spiked value have shown that the employed algorithms can be used for the direct determination of LABS and OB without need for separation. Also, comprehensive comparison of trilinear second-order calibration algorithms has been studied for PARAFAC, ATLD, SWATLD and APTLD. PARAFAC algorithm converged slowly but can afford the reasonable unique results, if the correct component number was selected. The ATLD can be performed in the presence of unknown interferences to provide more satisfactory concentration predictions. This algorithm has a capability to converge faster than the other algorithms. Indeed, it is insensitive to the component number. These recoveries values were in acceptable range for such samples and showed this method can provide solutions with acceptable accuracy for all analytes present in the samples. In this study, the performance of APTLD is very stable when the value of the penalty factors is greater than 10^8 and close to SWATLD. Both of these algorithms are also insensitive to component number and hold very fast convergence speed.

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Figure captions

Fig. 1. An example of the raw EEM of laundry powder sample before (A) and after (B) scattering areas removal

Fig. 2. Emission (A) and excitation (B) loadings obtained from PARAFAC algorithm

Fig. 3. PARAFAC emission (A) and excitation (B) loadings for waste water sample

Fig. 4. Emission (A) and excitation (B) loadings obtained from PARAFAC algorithm for agricultural soil sample

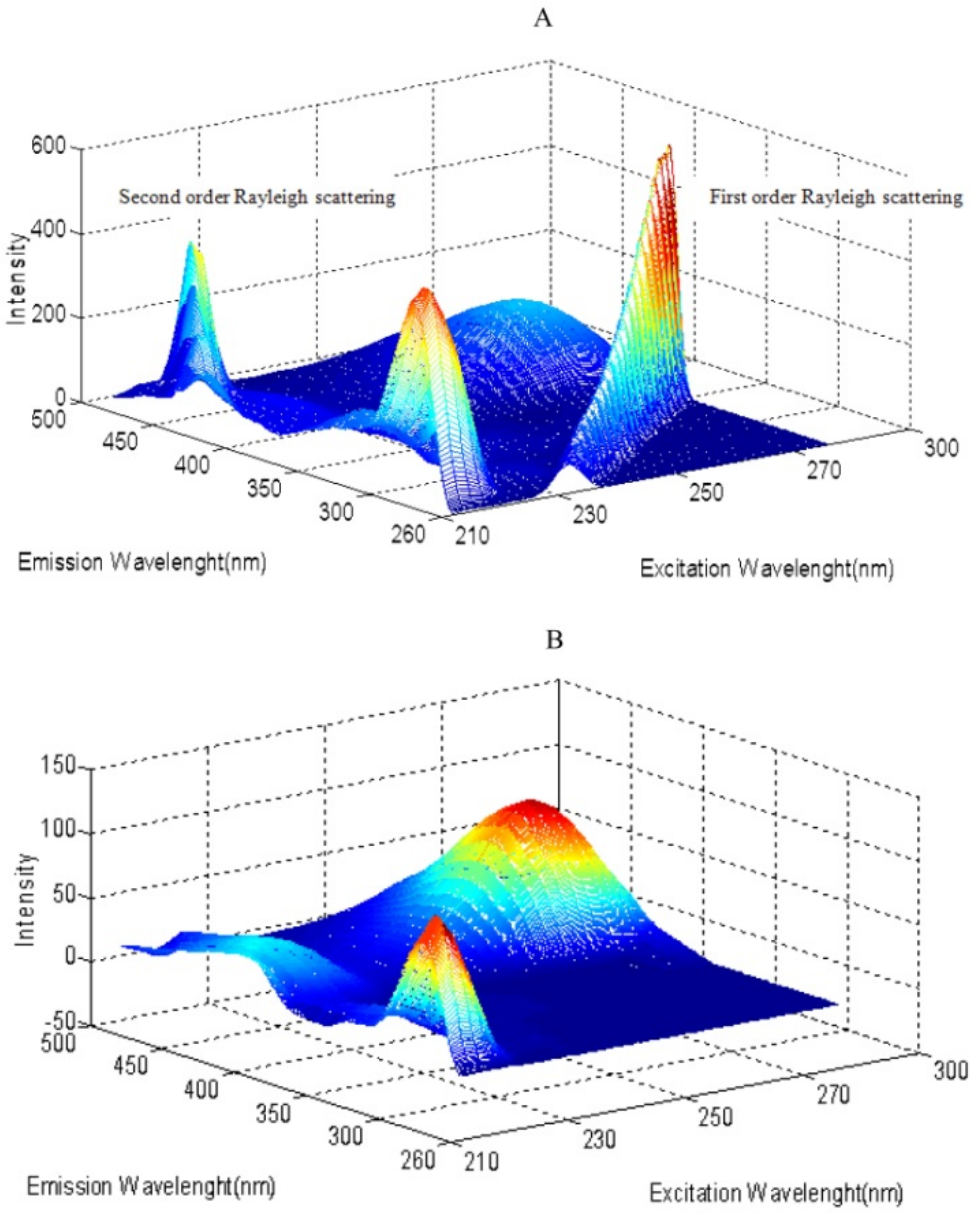


Fig. 1

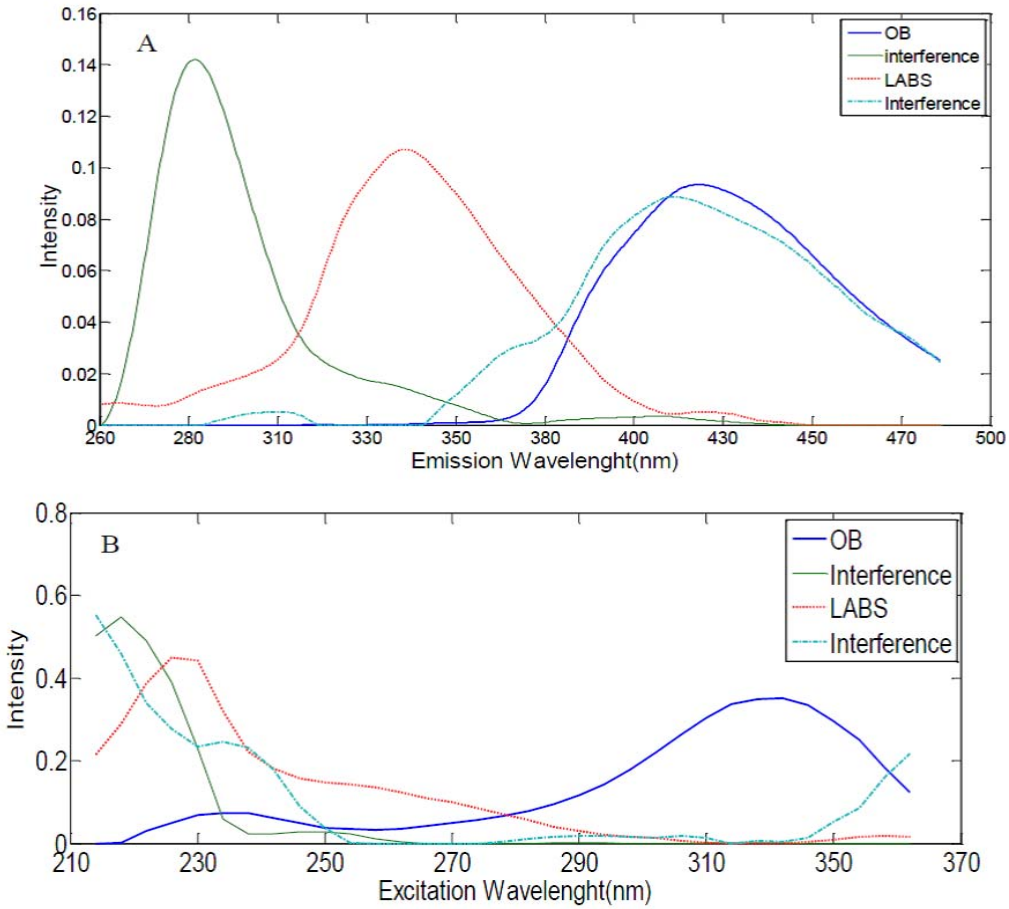


Fig. 2

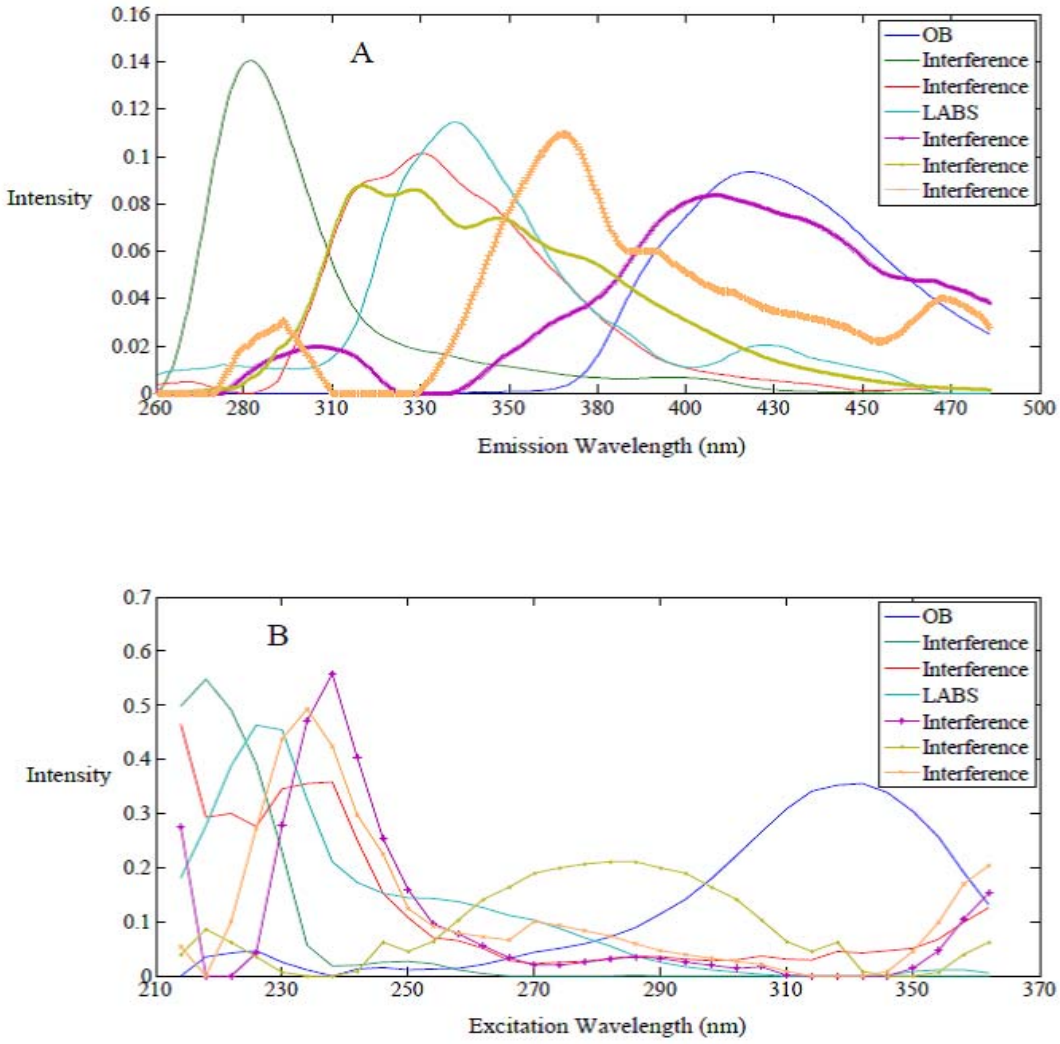
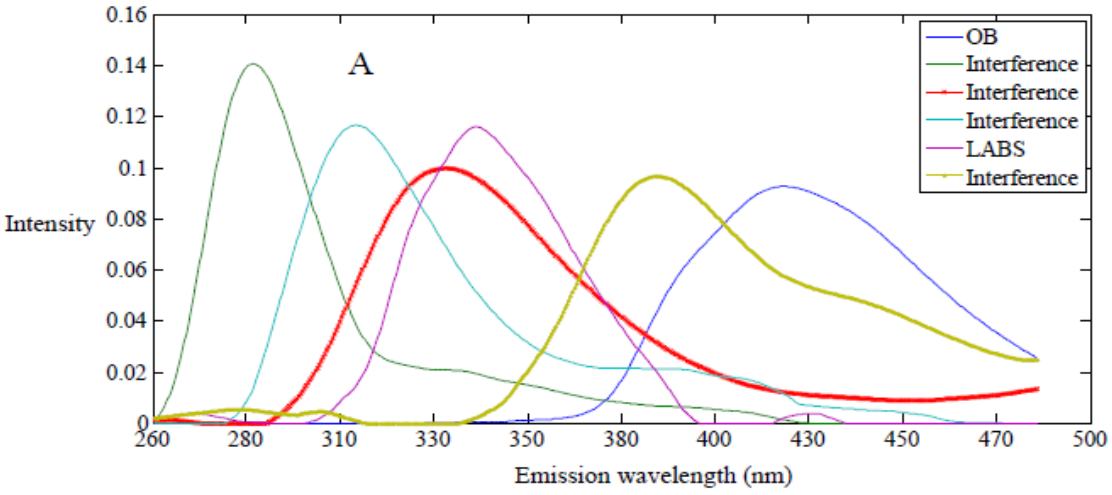


Fig. 3



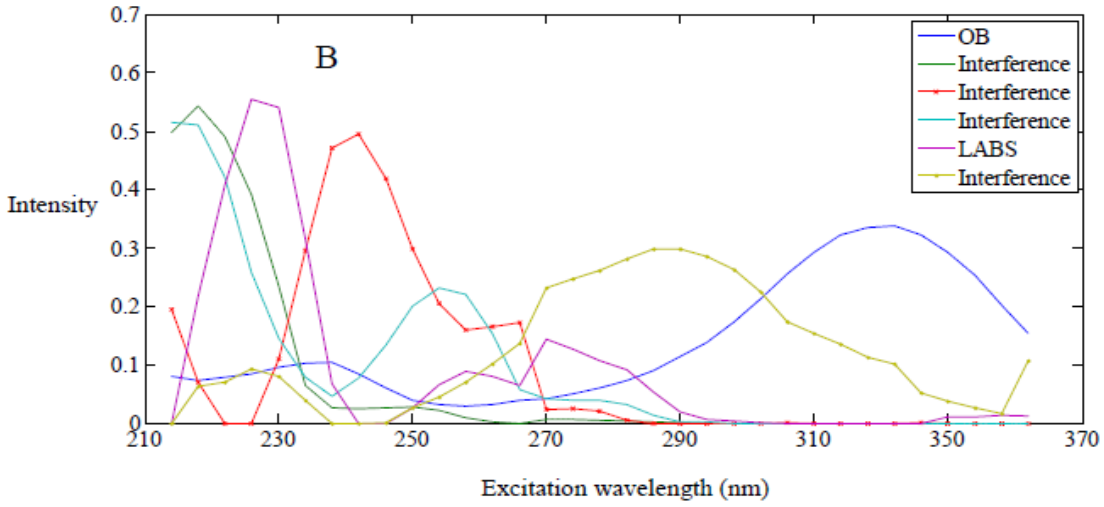


Fig. 4

Table captions

Table. 1 Obtained results from different methods in determining the number of components

Table. 2 Quantitative analysis of LABS and OB in the real samples

Table. 3 The assessment of LABS and OB in laundry powder with three way methods

Table. 4 Recovery experiment for mixtures of LABS and OB in waste water and soil samples

Table. 5 Figures of merit obtained from the multivariate calibration procedure in real sample analysis

Table 1 Obtained results from different methods in determining the number of components

Sample	Number of components	CORCONDIA /%	SD of residual	Cross validation
Laundry powders	1	100.00	10.2	20
	2	99.89	7.6	10
	3	93.74	4.5	6
	4	63.81	2.8	2
	5	0.41	2.8	2
Waste water	1	100.00	37	25
	2	99.89	13	17
	3	88.14	5	15
	4	84.72	2.9	10
	5	73.73	1.9	7
	6	72.19	1.7	5
	7	57.24	1.2	3
	8	6.60	1.2	3
Soil	1	100.00	43	23
	2	99.89	21	15
	3	99.71	7.2	11
	4	66.34	5.2	6
	5	58.71	2.7	4
	6	50.22	1.8	1
	7	-0.001	1.7	1

Table 2 Quantitative analysis of LABS and OB in the real samples

	Method	OB/% (±SD)	LABS/% (±SD)
Sample 1	PARAFAC	$5.0\times10^{-2}\pm1.0\times10^{-3}$	8.50±0.03
	APTLD	$5.0\times10^{-2}\pm1.0\times10^{-3}$	8.00±0.01
	SWATLD	$5.0\times10^{-2}\pm1.0\times10^{-3}$	8.10±0.01
	ATLD	$5.0\times10^{-2}\pm1.0\times10^{-3}$	9.00±0.03
Sample 2	PARAFAC	$5.0\times10^{-2}\pm1.0\times10^{-3}$	8.50±0.04
	APTLD	$5.0\times10^{-2}\pm1.0\times10^{-3}$	6.50±0.01
	SWATLD	$5.0\times10^{-2}\pm1.0\times10^{-3}$	7.00±0.01
	ATLD	$5.0\times10^{-2}\pm1.0\times10^{-3}$	9.00±0.03
Waste water	PARAFAC	$1.12\times10^{-4}\pm1.20\times10^{-5}$	0.052±0.006
	APTLD	$1.10\times10^{-4}\pm7.00\times10^{-6}$	0.060±0.011
	SWATLD	$1.10\times10^{-4}\pm7.00\times10^{-6}$	0.060±0.011
	ATLD	$1.06\times10^{-4}\pm6.00\times10^{-6}$	0.052±0.006
Soil	PARAFAC	$5.13\times10^{-5}\pm5.60\times10^{-6}$	$3.41\times10^{-4}\pm7.20\times10^{-5}$
	APTLD	$5.00\times10^{-5}\pm5.20\times10^{-6}$	$3.34\times10^{-4}\pm7.00\times10^{-5}$
	SWATLD	$5.00\times10^{-5}\pm5.20\times10^{-6}$	$3.34\times10^{-4}\pm7.00\times10^{-5}$
	ATLD	$6.31\times10^{-5}\pm1.10\times10^{-6}$	$3.82\times10^{-4}\pm2.20\times10^{-5}$

Table 3 The assessment of LABS and OB in laundry powders with three way methods

	Method	Added LABS /mgL^{-1}	Found LABS /mgL^{-1} (±SD)	Recovery /%	Added OB /μg L^{-1}	Found OB /μg L^{-1} (±SD)	Recovery /%
Sample 1	PARAFAC	0.0	1.7(±0.1)	-	0.0	0.9(±0.1)	-
		0.5	2.3(±0.3)	104.5	1.5	2.5(±0.2)	104.2
		1.0	2.8(±0.1)	103.7	1.0	2.0(±0.2)	105.2
		2.0	3.9(±0.1)	105.4	2.5	3.3(±0.1)	97.1
	Average recovery%			104.5±0.1			102.2±0.3
	APTLD	0.0	1.6(±0.0)	-	0.0	0.9(±0.1)	-
		0.5	2.1(±0.0)	100.0	1.5	2.4(±0.2)	100.0
		1.0	2.5(±0.1)	96.2	1.0	2.0(±0.1)	105.2
		2.0	3.8(±0.2)	105.5	2.5	3.3(±0.1)	97.1
	Average recovery%			100.6±0.3			100.8±0.2
	SWATLD	0.0	1.6(±0.0)	-	0.0	0.9(±0.1)	-
		0.5	2.1(±0.0)	100.0	1.5	2.4(±0.2)	100.0
		1.0	2.5(±0.1)	96.2	1.0	2.0(±0.1)	105.2
		2.0	3.8(±0.2)	105.5	2.5	3.3(±0.1)	97.1
	Average recovery%			100.6±0.3			100.8±0.2
	ATLD	0.0	1.9(±0.2)	-	0.0	0.9(±0.1)	-
		0.5	2.5(±0.3)	104.2	1.5	2.4(±0.2)	100.0
		1.0	2.8(±0.1)	96.5	1.0	2.0(±0.1)	105.2
		2.0	3.8(±0.2)	97.5	2.5	3.3(±0.1)	97.1
	Average recovery%			99.4±0.3			100.8±0.2
Sample 2	PARAFAC	0.0	1.7(±0.1)	-	0.0	0.9(±0.1)	-
		1.0	2.8(±0.2)	103.7	1.0	2.0(±0.1)	105.3
		1.5	3.1(±0.1)	96.9	0.5	1.5(±0.1)	107.1
		3.0	4.4(±0.3)	93.6	2.5	3.3(±0.1)	97.1
	Average recovery%			98.1±0.3			103.2±0.3
	APTLD	0.0	1.3(±0.3)	-	0.0	0.9(±0.1)	-
		1.0	2.5(±0.2)	108.7	1.0	2.0(±0.1)	105.3
		1.5	2.6(±0.3)	93.0	0.5	1.5(±0.1)	107.1
		3.0	4.7(±0.2)	109.3	2.5	3.3(±0.1)	97.1
	Average recovery%			103.7±0.5			103.2±0.3
	SWATLD	0.0	1.2(±0.3)	-	0.0	0.9(±0.1)	-
		1.0	2.4(±0.2)	109.0	1.0	2.0(±0.1)	105.3
		1.5	2.6(±0.3)	93.0	0.5	1.5(±0.1)	107.1
		3.0	4.4(±0.2)	104.7	2.5	3.3(±0.1)	97.1
	Average recovery%			103.7±0.5			103.2±0.3
	ATLD	0.0	1.8(±0.1)	-	0.0	0.9(±0.1)	-
		1.0	2.6(±0.3)	92.8	1.0	2.0(±0.1)	105.3
		1.5	3.2(±0.1)	97.0	0.5	1.5(±0.1)	107.1
		3.0	5.0(±0.1)	104.2	2.5	3.3(±0.1)	97.1
	Average recovery%			98.0±0.4			103.2±0.3

Table 4 Recovery experiment for mixtures of LABS and OB in waste water and soil samples

	Method	Added LABS /mgL^{-1}	Found LABS /mgL^{-1} (±SD)	Recovery /%	Added OB /μg L^{-1}	Found OB/μgL^{-1} (±SD)	Recovery /%
Waste water	PARAFAC	0.0	3.5(±0.1)	-	0.0	4.3(±0.2)	-
		1.0	4.4(±0.2)	97.8	0.0	4.4(±0.2)	102.3
		2.0	5.4(±0.1)	98.2	0.5	4.6(±0.1)	96.0
		4.0	8.1(±0.2)	108.0	1.0	5.0(±0.2)	94.3
	Average recovery%			101.3±0.3			97.5±0.2
	APTLD	0.0	3.6(±0.1)	-	0.0	4.3(±0.1)	-
		1.0	4.5(±0.1)	97.8	0.0	4.3(±0.0)	100.0
		2.0	5.9(±0.2)	105.4	0.5	4.7(±0.1)	98.0
		4.0	8.0(±0.1)	105.3	1.0	5.2(±0.1)	98.1
	Average recovery%			102.8±0.2			98.7±0.1
	SWATLD	0.0	3.6(±0.1)	-	0.0	4.3(±0.1)	-
		1.0	4.5(±0.1)	97.8	0.0	4.3(±0.0)	100.0
		2.0	5.9(±0.2)	105.4	0.5	4.7(±0.1)	98.0
		4.0	8.0(±0.1)	105.3	1.0	5.2(±0.1)	98.1
	Average recovery%			102.8±0.2			98.7±0.1
	ATLD	0.0	3.5(±0.1)	-	0.0	4.4(±0.1)	-
		1.0	4.9(±0.3)	108.9	0.0	4.3(±0.1)	97.7
		2.0	5.6(±0.1)	101.8	0.5	4.6(±0.2)	94.0
		4.0	8.2(±0.3)	109.3	1.0	5.1(±0.2)	94.4
	Average recovery%			106.7±0.2			95.4±0.3
Soil	PARAFAC	0.0	2.4(±0.1)	-	0.0	2.1(±0.2)	-
		0.5	2.6(±0.4)	90.0	0.5	2.5(±0.1)	96.1
		1.0	3.6(±0.2)	105.9	2.0	4.2(±0.1)	102.4
		2.0	4.6(±0.1)	104.5	2.5	4.9(±0.3)	106.5
	Average recovery%			100.1±0.5			101.7±0.3
	APTLD	0.0	2.3(±0.1)	-	0.0	1.8(±0.1)	-
		0.5	2.6(±0.2)	93.0	0.5	2.3(±0.0)	100.0
		1.0	3.6(±0.2)	109.0	2.0	4.0(±0.1)	105.3
		2.0	4.6(±0.1)	107.0	2.5	4.6(±0.1)	107.0
	Average recovery%			103.0±0.5			104.1±0.2
	SWATLD	0.0	2.3(±0.1)	-	0.0	1.8(±0.1)	-
		0.5	2.6(±0.2)	93.0	0.5	2.3(±0.0)	100.0
		1.0	3.6(±0.2)	109.0	2.0	4.0(±0.1)	105.3
		2.0	4.6(±0.1)	107.0	2.5	4.6(±0.1)	107.0
	Average recovery%			103.0±0.5			104.1±0.2
	ATLD	0.0	2.6(±0.3)	-	0.0	2.5(±0.1)	-
		0.5	2.9(±0.2)	93.5	0.5	3.1(±0.1)	103.3
		1.0	3.9(±0.2)	108.3	2.0	4.7(±0.1)	104.4
		2.0	4.9(±0.1)	106.5	2.5	5.4(±0.1)	108.0
	Average recovery%			102.3±0.5			105.2±0.1

Table 5 Figures of merit obtained from the multivariate calibration procedure in real sample analysis

			LABS	OB
Laundry powder	PARAFAC	Sensitivity	198.7	1482.8
		Precision	0.30	0.47
		Detection Limit	0.45	0.15
	APTLD	Sensitivity	332.7	1523.0
		Precision	0.15	0.45
		Detection Limit	0.21	0.07
	SWATLD	Sensitivity	331.8	1518.8
		Precision	0.15	0.45
		Detection Limit	0.21	0.07
	ATLD	Sensitivity	204.2	1569.9
		Precision	0.20	0.42
		Detection Limit	0.35	0.08
Waste water	PARAFAC	Sensitivity	718.1	1465.8
		Precision	0.48	0.32
		Detection Limit	1.43	0.98
	APTLD	Sensitivity	547.7	1495.9
		Precision	0.54	0.32
		Detection Limit	1.41	1.00
	SWATLD	Sensitivity	547.7	1495.9
		Precision	0.54	0.32
		Detection Limit	1.41	1.00
	ATLD	Sensitivity	692.9	1560.7
		Precision	0.67	0.43
		Detection Limit	1.53	0.98
Soil	PARAFAC	Sensitivity	713.3	1631.9
		Precision	0.49	0.35
		Detection Limit	1.45	1.00
	APTLD	Sensitivity	558.3	1474.4
		Precision	0.57	0.33
		Detection Limit	1.49	1.00
	SWATLD	Sensitivity	558.1	1474.4
		Precision	0.57	0.33
		Detection Limit	1.49	1.00
	ATLD	Sensitivity	679.7	1562.9
		Precision	0.51	0.33
		Detection Limit	1.53	1.00