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Baseline correction for Raman spectra using an improved asymmetric least squares method†

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Baseline shifts exist in many types of Raman spectrometers. Acquired spectra normally contain the desired signals as well as undesirable elements such as background noise. In this paper, an improved asymmetric least squares (IAsLS) method has been proposed for the baseline correction of Raman spectra. The baseline correction algorithm is initiated by the raw spectrum baseline, and this baseline can be estimated using a polynomial fitting method. For the simulated Raman spectra, the performance of the proposed algorithm was evaluated and compared with the asymmetric least squares (AsLS) method and Jiang's method. The results showed that it is improved by sixteen fold and nine fold respectively. This proposed IAsLS method was successfully applied to practical Raman spectral data and the results in the paper indicate that the baseline of Raman spectra can be automatically subtracted.

1. Introduction

Raman spectroscopy is a rapid analytical technology and it provides detailed spectroscopic fingerprint information of target molecules. This technique is powerful and non-destructive, which requires only minimal sample preparation and it can realize the online analysis. Therefore, it has been widely applied in food science, materials, chemistry, biochemistry and other fields for qualitative or quantitative analytical purposes. However, in many types of Raman spectrometers, the presence of unstable baselines is usually observed.[1–3] Obtained spectra often consist of the desired signal as well as undesirable elements such as background noise from the sample holder, instrument and sample themselves. The baseline may lead to serious problems if the data recorder reaches the detection limits during the practical operation. Moreover, baseline correction is important since this step extracts the true Raman peak intensities, which are necessary for further numerical processing. In addition, different baseline correction methods have unique, strict requirements.

Specifically, baseline correction methods vary according to the precision acquired, and the patterns of losing and computing times obtained.[4–7] Therefore, an algorithm can be applied for the selection of a baseline correction method which is suitable for a given Raman spectrum. A large number of baseline correction methods are utilized by research scientists, such as differencing and filtering, interpolation fitting, manual or automatic polynomials, using an asymmetric function[8,9] and the combination of methods mentioned above.[10] Currently, the baseline correction methods used are semi-manual, subjective, time consuming and lack repeatability.

The linear and constant drifts can be eliminated by using the differencing method.[11] However, the differencing method may amplify the high frequency noise in a Raman spectrum as well. Secondly, the interpolation fitting method requires the automatic selection of the interpolation node and this is dependent on the artificial experience.[12,13] The baseline fitting is not the same in different interpolation functions. For the case of a wavelet transform,[14,15] it is important to choose the optimal decomposition, and appropriate wavelet and threshold values. These values can be employed to distinguish between the high frequency noise, the low frequency baseline and the middle frequency signals. Both manual and automatic polynomial fitting methods[16] require the user to manually identify the 'non-Raman' locations, and determine the order of the polynomial, then the baseline curve is formed by fitting with these locations. The asymmetric least squares (AsLS)[17] method combines a smoother with the asymmetric weighting of deviations from the smooth trend to form an effective baseline estimation method. However, the limitation of this algorithm is that only the smoothness constraint with the second derivative is considered. In practice, the method requires that the baseline fits the raw data well, and that the first derivative is very close. Therefore, based on the AsLS method, Jiang proposed an asymmetric least squares method which also considered the first derivative constraint term and the background values as the initial baseline (it is described in ref. 18 and abbreviated as JAsLS).

An extensive literature review has been provided by Eilers and Schulze *et al.*,[15,19] which summarize the preprocessing

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methods for typical spectral backgrounds, without focusing on any particular instrumental method. Based on the advantages of AsLS and polynomial fitting, an improved asymmetric least squares (IAsLS) method is proposed in this paper. Then, this hypothesized method is employed to remove the background noise of practical Raman spectra.

2. Theory

2.1 The asymmetric least squares (AsLS) method

Based on the Whittaker smoother,[20] an asymmetric least squares (AsLS) method was proposed for background removal by Eilers.[19] A given vector $y = \{y_1, y_2, \ldots, y_i\}$ is defined as i, the observed frequency domain spectral intensities. The smoothing series $z = \{z_1, z_2, \ldots, z_i\}$ is faithful to y. Then, the penalized least squares function is minimized:

$$F = \sum_i (y_i - z_i)^2 + \lambda \sum_i \left(\Delta^2 z_i\right)^2 \quad (1)$$

with $\Delta^2 z_i = (z_i - z_{i-1}) - (z_{i-1} - z_{i-2}) = z_i - 2z_{i-1} + z_{i-2}$, $i \in [1, 2, 3, \ldots, m]$, Δ is a second-order differential operator. The parameter λ is introduced to tune the balance between the smoothness and fitness. Finally, the vector w is defined as the weights of fitness and the minimized function is introduced as follows:

$$F = \sum_i w_i (y_i - z_i)^2 + \lambda \sum_i \left(\Delta^2 z_i\right)^2 \quad (2)$$

The minimization of eqn (2) can lead to the following equation:

$$(W + \lambda D^T D)z = Wy \quad (3)$$

with $W = \mathrm{diag}(w)$, W is the diagonal matrix for vector w, T describes the transpose of a matrix, and D is the second order differential matrix: $Dz = \Delta^2 z$.

Generally, a lighter smoothing is capable of removing the noise, otherwise, stronger smoothing can eliminate the true signal. In order to estimate the true background, much more attention should be paid to the deviations in the positive direction for baseline correction. However, the weights of both negative and positive residuals y–z are the same when using the Whittaker smoother. Therefore, a key parameter of asymmetric least squares for baseline correction, p ($0 < p < 1$), is introduced and computed as follows: $w_i = p$ if $y_i > z_i$ and $w_i = 1 - p$ otherwise.

2.2 The improved asymmetric least squares (IAsLS) method

The limitation of AsLS is that it only considers the smoothness constraint with regards to the second derivative. In practice, on the premise of baseline smoothness, the baseline correction method requires that the baseline is well fitted, and that the first derivatives for baseline data are close to each other. Therefore, the penalized least squares function of the improved asymmetric least squares proposed in this paper is minimized and shown as follows:

$$F = \sum_i (y_i - z_i)^2 + \lambda_1 \sum_i (\Delta(y_i - z_i))^2 + \lambda \sum_i \left(\Delta^2 z_i\right)^2 \quad (4)$$

where $\Delta(y_i - z_i) = (y_i - z_i) - (y_{i-1} - z_{i-1}) = y_i - y_{i-1} - (z_i - z_{i-1})$, $\Delta^2 z_i = (z_i - z_{i-1}) - (z_{i-1} - z_{i-2}) = z_i - 2z_{i-1} + z_{i-2}$. The first two parts in F measure the fit to the signal and the fit to the first derivative of the signal respectively, however, the rest is a penalty on the non-smooth behavior of z. The balance between the three parts is tuned by the parameters λ_1 and λ. Finally, the vector of weights, w, is introduced and the minimized function is as follows:

$$F = \sum_i [w_i (y_i - z_i)]^2 + \lambda_1 \sum_i (\Delta(y_i - z_i))^2 + \lambda \sum_i \left(\Delta^2 z_i\right)^2 \quad (5)$$

The minimization of eqn (5) can lead to the following equation:

$$(W^T W + \lambda_1 D_1^T D_1 + \lambda D^T D)z = (W^T W + \lambda_1 D_1^T D_1)y \quad (6)$$

with $W = \mathrm{diag}(w)$, and the weight coefficient w is defined the same as for AsLS. $D_1 = \Delta(y - z)$ and $Dz = \Delta^2 z$ are first and second order differential matrices respectively.

Because of the mutual interaction of the weights and smooth curves, the solution for the equations seems complicated. However, it can be transformed into two easy computations in an iterative application. At the same time, the estimation values of the initial baseline background for the raw spectrum are very important for the improved asymmetric least squares algorithms. Compared with background values estimated using the JAsLS method, the initial baseline background was estimated using the polynomial fitting method in this paper. The flow chart of the IAsLS algorithm is shown in Fig. 1.

The initial baseline of the raw spectrum y is fitted by second order polynomials, say $z^{(0)}$. According to $z^{(0)}$, it is easy to compute new weights, say $w^{(0)}$. Based on these weights, a new estimate of z is obtained by solving eqn (6). Then, we repeat these steps until the weights become constant.

Eilers[19] reported that, for an initial baseline estimation, the algorithm above can achieve convergence in about 5 to 10 iterations. However, it may not be able to estimate the signal background completely. Hence, the proposed algorithm is working iteratively. The residual of the baseline is reflected in the spectral background. Therefore, the spectrum is updated by the residual spectrum in the next iteration, and then repeats the estimation of the baseline with a polynomial fitting. When the residual of the baseline is almost unchanged in two continuous iterations, then the algorithm terminates. Using this method, algorithm convergence can be obtained as the iterations always go downhill with the gradient direction. It is described by simulated spectra in detail in Fig. 3.

2.3 Programming and software

All programs were written using Matlab R2011band run on Windows 7 on a personal computer (RAM 4G, CPU 2.83 GHz). The real Raman spectra were obtained from an Ocean Optic Peak Seeker Pro Raman spectrometer 25 equipped with a TE-cooled CCD detector, and 785 nm radiation from a diode laser with a power of 300 mW for sample excitation.

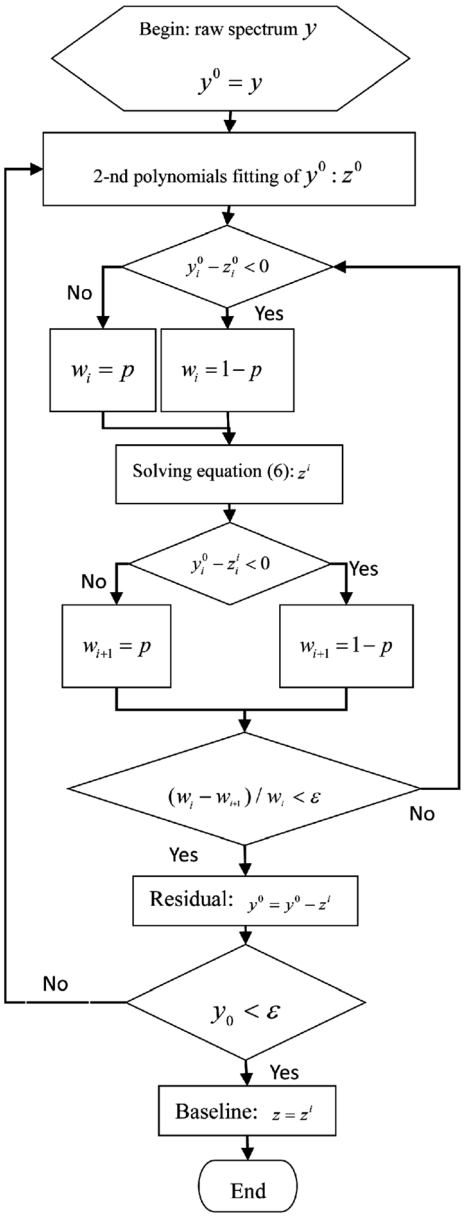

Fig. 1 The flow chart of the IAsLS algorithm.

3. Applications

Normally, there are many types of background noise origins including Rayleigh scattering, long and short Stokes shift fluorescence, sample holder and instrument effects in the Raman spectra. The fluorescence effects exist as three smooth features which are a function of Raman shifts. These features include offset and linear baselines, and exponential curves. Sometimes, the fluorescence background is so strong that it overlaps with the peaks of the Raman spectrum. Furthermore, removing fluorescence background with high intensity will lead to a lower signal-to-noise ratio, because the Raman peaks could be weakened as well. The baseline shifts could be different from spectrum to spectrum, even for the same samples. Therefore, inconsistent baselines may lead to an increasing of complexity

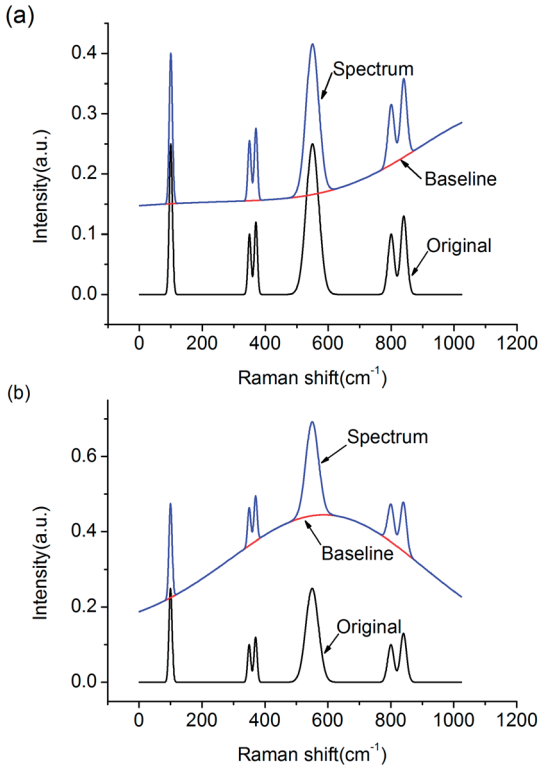

Fig. 2 The simulated spectra with complex baseline backgrounds. (a) Baseline 1 and (b) baseline 2.

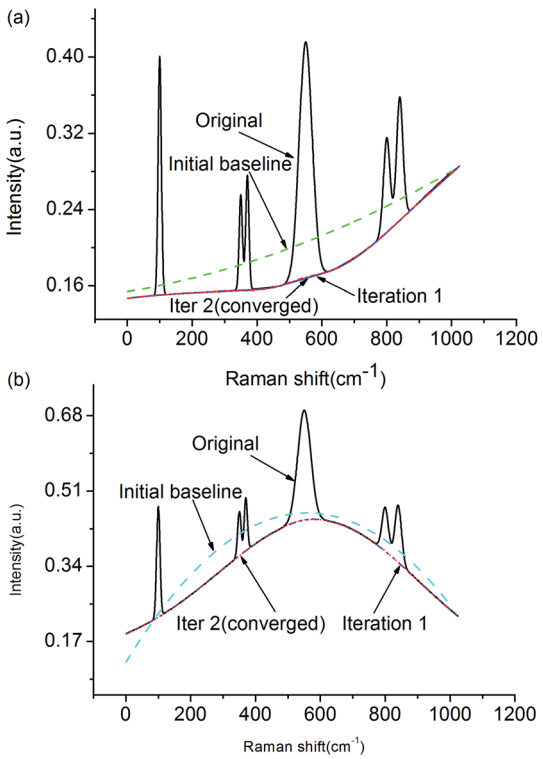

Fig. 3 Iteratively estimated baselines by IAsLS of simulated Raman spectra.

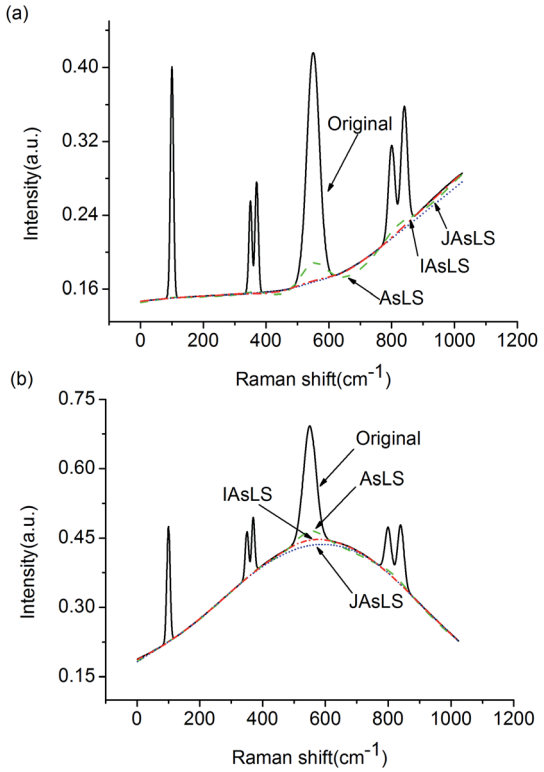

Fig. 4 The performances of baseline corrections based on AsLS, JAsLS and IAsLS. (a) Baseline 1 and (b) baseline 2.

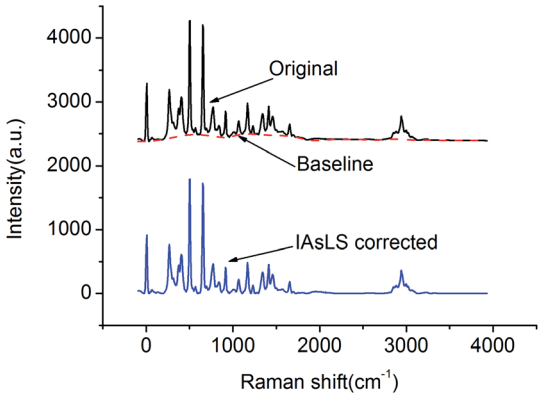

Fig. 5 Original spectrum and the estimated baseline of dimethoate solution by the IAsLS baseline correction method ($\lambda = 10^2$, $\lambda_1 = 10^{-5}$, $p = 0.001$).

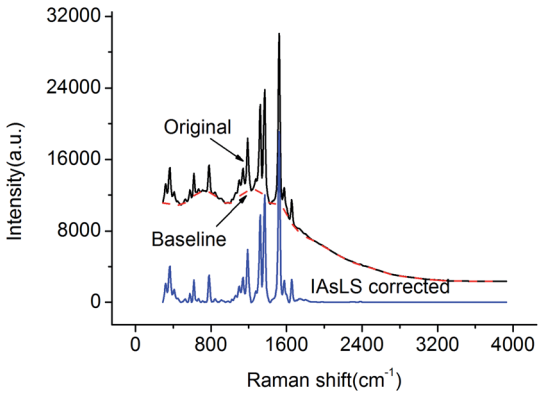

Fig. 6 Original spectrum and the estimated baseline of solid Rhodamine 6G by the IAsLS baseline correction method ($\lambda = 10^2$, $\lambda_1 = 10^{-5}$, $p = 0.01$).

and a decreasing of applicability of mathematical models for qualitative and quantitative analysis.

To obtain a better performance from the baseline correction algorithm, we computed the optimal values for the parameters p, λ_1 and λ, with the true baseline, say b, as a reference. The Root Mean Square Error (RMSE) is minimized using the parameters p, λ_1 and λ which were varied on a fine grid as follows:

$$\mathrm{RMSE} = \sqrt{\sum_i \left(b_i - b_i^0\right)^2 \Big/ n} \qquad (7)$$

We don't know b in reality, but it can provide us a value for the optimal performance case, and it is worthwhile for us to find the optimal parameters for algorithms if the RMSE can be made smaller.

The simulation was carried out in order to imitate real spectral data sets that contain various backgrounds and Raman signals. A broader Gaussian peak was treated as the curved background, a linear function was treated as the sloping background, and a narrower Gaussian peak was treated as the spectrum of interest. The simulated Raman spectra consisted of 1024 channels. The amplitudes of the simulated spectra were 0.25, 0.1, 0.12, 0.25, 0.1, 0.13. The slope of the linear part of the baseline was set to 0.00001. The amplitudes of the background curves were 0.15, 0.20 (baseline 1) and 0.15, 0.30 (baseline 2) respectively. The two simulated spectra which include representative features such as overlapping peaks and high fluorescence backgrounds are shown in Fig. 2.

First, the convergence of the IAsLS baseline correction algorithm is shown in Fig. 3. The two iterations and the final

Table 1 Performances of different baseline correction algorithms

		Baseline 1			Baseline 2		
Algorithms	Parameters	Time(s)	Iterations	RMSE	Time(s)	Iterations	RMSE
AsLS	$\lambda = 10^4$	0.0468	—	0.0064	0.0156	—	0.0064
JAsLS	$\lambda = 10^{-2}$	0.1092	3	0.0032	0.0156	2	0.0038
IAsLS	$p = 0.001$	0.2652	2	0.0006	0.2964	2	0.0004

results of the IAsLS algorithm on the simulated Raman spectra are demonstrated, and convergence occurs after 2 iterations. The initial estimated baselines, which were fitted by second order polynomials, were strongly improved by the new iterations. Therefore, the convergence of the IAsLS baseline correction method was verified.

Then, considering the range of the parameters in ref. 18, by choosing proper parameters ($\lambda = 10^4$, $\lambda_1 = 10^{-2}$, $p = 0.001$), the performance of the IAsLS baseline correction was compared with AsLS and JAsLS, and the results are shown in Fig. 4. It was found that the background of the raw spectrum was over-fitted by the AsLS algorithms and that the intensity of spectrum was weakened as well (500–600 cm^{-1} in baseline 1 and baseline 2). In addition, the JAsLS method did not fit the background well at 800–1000 cm^{-1} (baseline 1), 0–100 cm^{-1} (baseline 2), and 500–700 cm^{-1} (baseline 2). However, it fit similarly to the IAsLS method at 100–800 cm^{-1} (baseline 1), 100–500 cm^{-1} (baseline 2), and 700–800 cm^{-1} (baseline 2). Finally, in summary, using the proposed IAsLS method, the baseline background was fitted well for the whole Raman spectral range.

In addition, compared with the three algorithms in Table 1, the computation time of AsLS was equal or shorter than JAsLS, but was the longest for RMSE. The computation times of JAsLS and IAsLS were equal or longer compared with AsLS. However, they were all less than one second, which doesn't affect the offline or online baseline corrections of Raman spectra. The RMSEs of the proposed IAsLS algorithm were the least, only 0.0006 (baseline 1) and 0.0004 (baseline 2) respectively. They were reduced by five fold and eleven fold compared with JAsLS and AsLS respectively for the simulated Raman spectrum (baseline 1), and nine fold and sixteen fold compared with JAsLS and AsLS respectively for the simulated Raman spectrum (baseline 2). In addition, iterations of the IAsLS method were less than JAsLS (baseline 1). The simulation shows that, with proper parameters, the obtained results were quite near to the true baseline. Therefore, the validity of the IAsLS method was approved.

In practice, we only have the experimental data which can guide us in the choosing of suitable values for the parameters p, λ_1 and λ. Simultaneously, it has been difficult for us to find a fail-safe cross-validation algorithm yet. Therefore, we report here of our experience with relatively *ad hoc* computations. These can assist us in setting up approximately optimal parameters. Using the true baseline b, and the simulated spectrum (baseline 1) as a reference, we varied p, λ_1 and λ on a fine grid and the RMSE was calculated afterwards to obtain an appropriate range for the parameters.

For each of the parameters (p, λ_1 and λ), a baseline was estimated and the RMSE of the proposed method was computed. Simulation results for the choosing of suitable values for parameters p, λ_1 and λ are shown in the ESI (Fig. S1–S4†). The simulation shows that, in order to obtain the optimal performance, the value of p should be set to less than 0.1, and the range of λ from 10^2 to 10^6, and the value of λ_1 to less than 10^{-4}.

Now, we demonstrate two applications of the IAsLS baseline correction procedure. The examples given are of different complexity (overlapping peaks and high fluorescence backgrounds) and illustrate the performance and limitations of the algorithm.

Fig. 5 shows the IAsLS baseline correction result for a spectrum of dimethoate solution, with $\lambda = 10^2$, $\lambda_1 = 10^{-5}$, and $p = 0.001$. The raw spectrum consisting of 1024 Raman shift units was obtained from the Raman spectrometer. The spectrum exhibits a linear baseline which can be attributed to the glass substrate. The spectrum for dimethoate solution, with many overlapping peaks, was corrected well by IAsLS compared with other baseline correction methods (Fig. S5†). The IAsLS baseline correction result for a spectrum of solid Rhodamine 6G is shown in Fig. 6, with $\lambda = 10^2$, $\lambda_1 = 10^{-5}$, and $p = 0.001$. The spectrum exhibits a baseline disturbance that can be attributed to the fluorescence background of the sample. The results show that IAsLS was able to better remove the fluorescence signal compared with the other two methods, but was not over-fitted. Above all, both of these irrelevant spectral disturbances were removed well by the IAsLS baseline correction.

4. Conclusion

In this paper, we present an iterative method to estimate the backgrounds of Raman spectra. The simulation results show that the backgrounds of raw spectra are over-fitted by the AsLS algorithms and the intensity of spectra are weakened as well. In addition, the JAsLS method cannot fit backgrounds well at 800–1000 cm^{-1}, 0–100 cm^{-1} (baseline 2), and 500–700 cm^{-1} (baseline 2) for simulated spectra. However, it fits similarly to the IAsLS method at 100–800 cm^{-1} (baseline 1), 100–500 cm^{-1} (baseline 2), and 700–800 cm^{-1} (baseline 2). Finally, using the IAsLS method, the baseline background can be fitted well over the whole Raman spectral range. When the appropriate parameters were given, the simulation results indicated that the performance of the IAsLS algorithm was improved by nine fold and sixteen fold compared with that of JAsLS and AsLS respectively for the simulated Raman spectra. The actual Raman spectra experiments show that Raman peaks are eliminated automatically and only the baseline is subtracted. Furthermore, the position and shape of peaks can be maintained with their original forms with this proposed method.

Abbreviations

IAsLS	Improved asymmetric least squares
AsLS	Asymmetric least squares
RMSE	Root mean square error
JAsLS	Jiang's asymmetric least squares baseline correction method

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References

1 M. N. Leger and A. G. Ryder, *Appl. Spectrosc.*, 2006, **60**, 182–193.
2 A. F. Ruckstuhl, M. P. Jacobson, R. W. Field and J. A. Dodd, *J. Quant. Spectrosc. Radiat. Transfer*, 2001, **68**, 179–193.
3 H. F. Boelens, R. J. Dijkstra, P. H. Eilers, F. Fitzpatrick and J. A. Westerhuis, *J. Chromatogr. A*, 2004, **1057**, 21–30.
4 K. H. Liland, T. Almøy and B. H. Mevik, *Appl. Spectrosc.*, 2010, **64**, 1007–1016.
5 C. Rowlands and S. Elliott, *J. Raman Spectrosc.*, 2011, **42**, 363–369.
6 Ł. Komsta, *Chromatographia*, 2011, **73**, 721–731.
7 A. T. Weakley, P. R. Griffiths and D. E. Aston, *Appl. Spectrosc.*, 2012, **66**, 519–529.
8 V. Mazet, C. Carteret, D. Brie, J. Idier and B. Humbert, *Chemom. Intell. Lab. Syst.*, 2005, **76**, 121–133.
9 Z. M. Zhang, S. Chen and Y. Z. Liang, *Analyst*, 2010, **135**, 1138–1146.
10 C. V. Di Anibal, L. F. Marsal, M. P. Callao and I. Ruisánchez, *Spectrochim. Acta, Part A*, 2012, **87**, 135–141.
11 H. G. Schulze, R. B. Foist, K. Okuda, A. Ivanov and R. F. B. Turner, *Appl. Spectrosc.*, 2012, **66**, 757–764.
12 J. J. deRooi and P. H. C. Eilers, *Chemom. Intell. Lab. Syst.*, 2012, **117**, 56–60.
13 K. H. Liland, E.-O. Rukke, E. F. Olsen and T. Isaksson, *Chemom. Intell. Lab. Syst.*, 2011, **109**, 51–56.
14 Y. G. Hu, T. Jiang, A. G. Shen, W. Li, X. P. Wang and J. M. Hu, *Chemom. Intell. Lab. Syst.*, 2007, **85**, 94–101.
15 G. Schulze, A. Jirasek, M. M. Yu, A. Lim, R. F. Turner and M. W. Blades, *Appl. Spectrosc.*, 2005, **59**, 545–574.
16 F. Xinwei, Z. Zhongliang, S. Mengjie and C. Peisheng, *Comput. Appl. Chem.*, 2009, **6**, 020.
17 P. H. C. Eilers, *Anal. Chem.*, 2004, **76**, 404–411.
18 J. An, P. Jiangtao, X. Qiwei, W. Jiping and P. Silong, *Comput. Appl. Chem.*, 2012, **29**, 537–540.
19 P. H. C. Eilers and H. F. M. Boelens, *Baseline correction with asymmetric least squares smoothing*, Leiden University Medical Centre report, 2005.
20 P. H. C. Eilers, *Anal. Chem.*, 2003, **75**, 3631–3636.