Asian Journal of Chemistry; Vol. 24, No. 10 (2012), 4257-4262

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

# Transfer of Raman Spectra with Different Resolutions Applying Convolution with Gaussian Function

XUE-FENG DONG and LIAN-KUI DAI*

State Key Laboratory of Industrial Control Technology, Zhejiang University, Hangzhou 310027, Zhejiang Province, P.R. China

*Corresponding author: E-mail: lkdai@iipc.zju.edu.cn

(*Received*: 17 May 2011; *Accepted*: 30 April 2012) AJC-11366

Calibration transfer of Raman spectra was investigated on the basis of instrument response function, which is affected by the resolution of the spectrometer. A simplified procedure is presented allowing the transfer of Raman spectra from higher to lower resolution instruments (or conditions). Needn't to measure a set of well-prepared samples to construct a statistical transfer model, the method employed in preent study, a convolution step involving a Gaussian transfer function, which theoretically describes the instrumental difference from source to target. And with the help of established methods for wavenumber calibration and relative intensity correction, an integrated algorithm for Raman spectra transfer is provided. Two spectral experiments of three analytes were performed for certification: (1) Transfer on a Fourier transform (FT) Raman spectrometer under various resolution conditions; (2) Transfer between two dispersive Raman spectrometers equipped with charge-coupled device (CCD). In almost all cases, the correlation coefficient between the measured spectra and transferred spectra could reach to 0.99. It suggested that this procedure may be applicable for all kinds of Raman spectra transfer and even works universally in other spectroscopy.

**Key Words: Raman spectroscopy, Calibration transfer, Resolution, Voigt function, Gaussian transfer function.**

## INTRODUCTION

Raman spectroscopy is an established analytical technique utilized in academic research and industrial applications[1]. It is fast and noninvasive and provides fingerprint features of the analyte. The progress of Raman spectroscopy benefits from various multivariate calibration methods, such as partial least squares and support vector machines. Today, kinds of quantitative and qualitative calibration models have been developed to determine chemical compositions or physical properties. However, an existing model developed on one Raman spectrometer (referred to as primary or source instrument) becomes inapplicable when applied to spectra measured on another Raman spectrometer (referred to as secondary or target instrument)[2]. And variations in measurement environment due to resolution adjustment or component replacement also limit the application of previous models[3]. This is because the instrumental response function is different for a new instrument or measurement condition. Some subtle variations could be significant enough for a well-established model to have great prediction error of new samples. A traditional solution to this problem is to remeasure every sample and construct a new model, which requires considerable time, effort and cost. It's even impossible sometimes when the samples are chemically or physically unstable, hazardous, or difficult to prepare[4].

To avoid full recalibration, one alternative is to apply some chemometric methods to correct the instrumental or environmental variations. In some cases where the variation source and its mechanism can be identified, the strategy is to incorporate it into the calibration model. Some scholars proposed to build robust models whose prediction accuracy would not be affected by those variations[5,6]. The remaining researchers turn to calibration transfer methods to resolve the problem[7-9]. Several transfer algorithms were published, like direct standardization, piecewise direct standardization[10] and a patent algorithm by Shenk and Westerhaus[11]. These algorithms use the spectra of a few transfer samples measured on both instruments or under both environments, to determine a structured transfer model. Then the model can be used to transfer the spectra measured on one instrument to another instrument, enabling the calibration model in the new situation. Among those algorithms, piecewise direct standardization was reported to obtain a better result and widely applied in industrial field. The disadvantage of calibration transfer methods is that they need a set of transfer samples measured twice, which could be impractical sometimes. Transfer samples should be well chosen or prepared to have strong band information, or else the transfer model will be less effective.

Available literatures dealt with model transfer problem mostly in near-infrared (NIR) and UV-visible spectroscopy, and seldom in Raman spectroscopy. The main reason is that industrial applications of Raman technique have been limited to its difficulties and pricing[12]. Papers discussing calibration transfer in Raman adopted statistical methodologies, which were successfully utilized in near infrared and other spectroscopy. The study concern the instrument-to-instrument transfer based on the fundamental difference in instrumental response function. Theoretically, an individual peak from Raman scattering can be represented with a Voigt function, which is instrumental dependent. One major parameter constituting the Voigt function is the resolution, which is to evaluate the ability to distinguish two adjacent peaks. When the resolution is altered, both the peak widths and heights across the spectrum will be changed. Mann and Vickers proposed a convolution step to transfer spectra from a high-resolution instrument to a low-resolution instrument[13]. It does not need to measure a set of transfer samples, only a 'gun sight' convolution function should be determined. This function is empirically suggested by the authors and has two adjustable parameters, which complicate its application.

Inspired by the convolution idea, we proposed to employ a Gaussian function instead of the 'gun sight' function. The validity of Gaussian function for transfer will be verified based on the Voigt model of Raman peak. The only parameter to form the transfer function is the Gaussian width, which could be calculated from the resolutions of both source and target instruments. Besides resolution, spectral differences also exist in wavelength/wavenumber positions and intensities. In our work, a wavelength reference argon lamp is introduced for wavenumber calibration and a standard reference material SRM2241 is introduced to correct variation of relative intensity across the spectral range. Our spectra transfer between different instruments proceeds in the following sequence: (1) Wavenumber calibration; (2) Relative intensity correction; (3) Resolution transfer. An experimental verification is performed on a Fourier transform (FT) Raman spectrometer between spectra measured with different resolution. Another promising experiment is between two dispersive CCD Raman spectrometers from different manufactories.

## THEORY

Interpreted with the theory of molecular vibration, an individual Raman peak is Lorentzian in physics, with the line-profile given below[14]:

$$L(\nu) = L_0 \frac{\omega_L^2}{(\nu - \nu_0)^2 + \omega_L^2} \qquad (1)$$

where, $\nu$ is the wavenumber variable, $L_0$ is the peak height, $\nu_0$ is the center position and $\omega_L$ is the Lorentzian width. The Lorentzian line is ideal since it only expresses the natural interactions of the analyte. In practice, a real Raman spectrum is also determined by the configuration of the spectrometer employed. Only with a high-resolution monochromator or interferometer, the spectrometer effect could be ignored and the actual Lorentzian line profile could be recorded.

Due to instrumental effect (*e.g.*, the slit function) and Doppler effect (which is caused by a statistical distribution of velocities of atoms)[15], the Lorentzian profile is broadened with a Gaussian line-profile, which can be expressed as below:

$$G(\nu) = G_0 \exp\left[ -\left( \frac{\nu}{\omega_G} \right)^2 \right] \qquad (2)$$

where, $G_0$ refers to the height and $\omega_G$ refers to the Gaussian width.

Broadening with a Gaussian profile generates the well-known Voigt profile, which is a convolution of a Lorentzian and Gaussian profile. The expression of Voigt function is given by:

$$V(\nu) = \int_{-\infty}^{+\infty} L_0 \frac{\omega_L^2}{(\nu - \nu_0 - \nu')^2 + \omega_L^2} G_0 \exp\left[ -\left( \frac{\nu'}{\omega_G} \right)^2 \right] d\nu' \qquad (3)$$

or simplified as:

$$V = L * G \qquad (4)$$

where, symbol * represents the convolution operation. The Voigt function and some of its approximations have been widely used for curve fitting in applied spectroscopy and other fields of physics[16,17].

A Gaussian broadening of Lorentzian line is the Voigt line whose width is determined by both $\omega_L$ and $\omega_G$. Fig. 1 shows a Lorentzian profile and how it would be broadened with different Gaussian functions. It can be seen that the peak will drop and broaden as $\omega_G$ grows.

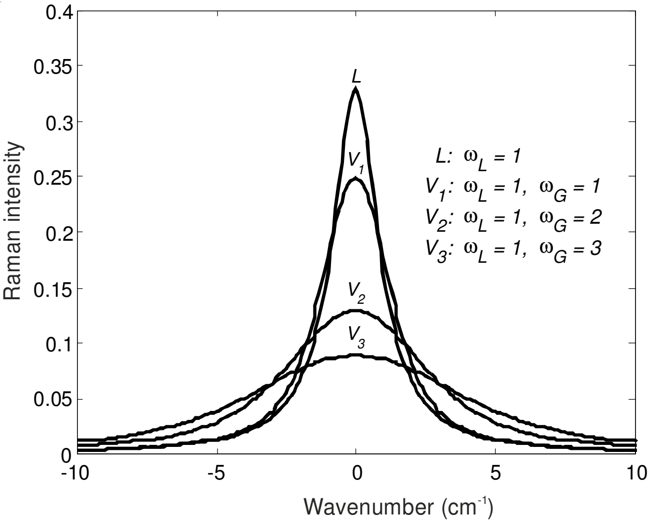

Fig. 1. Lorentzian profile and Voigt profiles broadened with different Gaussian functions. All profiles are normalized by $\int L d\nu = \int V_1 d\nu = \int V_2 d\nu = \int V_3 d\nu = 1$

The only instrumental parameter of the Voigt profile is the Gaussian width $\omega_G$, which indicates the resolution of a spectrometer. For a CCD Raman spectrometer, the resolution is mainly determined by the width of entrance slit and the reciprocal linear dispersion of the monochromator. For Fourier transform Raman spectrometer, it is determined by the maximum optical path difference and the apodization function[18]. The resolution of a Fourier transform spectrometer is adjustable in a wavenumber range, while that of a CCD spectrometer is fixed after assembling. In some cases, scholars prefer to visualize the resolution with full-width at half-height (FWHH), which is more convenient to read from a curve. The numerical relationship between them is:

$$\mathrm{FWHH} = \frac{2}{\sqrt{\ln 2}} w_G \quad (5)$$

For two spectrometers or two measurement circumstances A and B, the measured spectra of the same analyte can be denoted by $S_1$ and $S_2$ respectively. The Lorentzian profile is natural, which means this part contained in $S_1$ and $S_2$ is identical. The only difference lies in the Gaussian part, which is instrumental dependent. In theory, a Raman spectrum can be modeled as a linear superposition of a certain number of Voigt functions. And the Gaussian functions across the spectral range can be supposed to be identical. Therefore, $S_1$ and $S_2$ can be modeled as:

$$S_1 = \Sigma V_1 = \Sigma L*G_1;\ S_2 = \Sigma V_2 = \Sigma L*G_2 \quad (6)$$

Suppose that the spectral resolution of A is higher than B, which means the Gaussian width of $G_1$ is smaller than $G_2$. Based on the definition and nature of convolution, we learn that the convolution of two Gaussians is still a Gaussian function. Then we could find a Gaussian function G' satisfying the following requirement:

$$G_2 = G_1*G' \quad (7)$$

The width of G' satisfies:

$$\omega_{G'} = \sqrt{\omega_{G_2}^2 - \omega_{G1}^2} \quad (8)$$

where $\omega_{G_1}$, $\omega_{G_2}$ and $\omega_{G'}$ represent the Gaussian width of $G_1$, $G_2$ and G′ respectively, $\omega_{G_1} < \omega_{G_2}$. As a result, the Raman spectra can be transferred from $S_1$ to $S_2$ by convolution with G′, because:

$$S_2 = \Sigma L*G_2 = \Sigma L*(G_1*G') = (\Sigma L*G_1) * G = S_1*G \quad (9)$$

In principle, a Raman spectra collected with a higher resolution can be transferred to a lower resolution in the same wavenumber region. Without full formulation of the Raman spectra with Voigt functions, the only requirement is that the Gaussian transfer function $G'$ is provided. As in most Raman spectroscopy analysis, the relative intensity across the spectral range is considered. And a normalization procedure correcting the overall intensity would be applied. So the Gaussian transfer function could be simplified as:

$$G'(\nu) = \exp\left[-\left(\frac{\nu}{\omega_{G'}}\right)^2\right] \quad (10)$$

Therefore, only two parameters $\omega_{G_1}$ and $\omega_{G_2}$ should be acquired for transfer. In fact, the resolution parameters could be tested with spectral calibration sources such as argon or neon lamps. These light sources will emit Gaussian lines when excited.

## EXPERIMENTAL

Benzene was obtained from Zhejiang Juhua Xinlian Chemical Co. Ltd., cyclohexane was obtained from Aladdin Chemistry Co. Ltd. and *m*-xylene was obtained from Sinopharm Chemical Reagent Co. Ltd.

**Spectrometers:** Fourier transform Raman spectra were collected on a Bruker MultiRAM spectrometer using OPUS software. The FT-Raman spectrometer was equipped with a 500 mW Nd:YAG laser source emitting at 1064 nm and an InGaAs detector. It provides a Raman shift range of 3600-100 $cm^{-1}$.

And two dispersive CCD Raman systems have been assembled in sequence in our laboratory. They share the same 785 nm laser BRM-785, the same Raman probe BAC100-785 and the same cuvette holder BCR100A all obtained from B & W Tek, Inc.. The source instrument is based on a high resolution spectrometer BTC162E from B & W Tek, Inc., which is operated with a front-illuminated 2048 element liner CCD detector and a 25 μm wide slit. It covers a Raman shift wavenumber range of 0-2600 $cm^{-1}$ at approximately 1.3 $cm^{-1}$ interval. The target instrument is a spectrometer QE65000 from Ocean Optics, Inc., which is equipped with a back-illuminated 1024 × 58 element array CCD detector and a 50 μm wide slit. With this arrangement the Raman shift wavenumber range is 0-2100 $cm^{-1}$ at approximately 2 $cm^{-1}$ interval.

**Computations:** All algorithms were written with Matlab 7.8 on a Core II PC running Windows XP operating system. In order to facilitate calculation, the convolution was discretized in Matlab. To calculate discrete convolution precisely, the spectra data to be transferred and the Gaussian function should be interpolated with a relatively small step.

**Evaluation index:** To evaluate the effect of transfer, the correlation coefficient between two spectra (r) is chosen as the criterion. The definition of r is:

$$r = \frac{\mathrm{Cov}(X_1, X_2)}{\sqrt{\mathrm{Var}(X_1)\mathrm{Var}(X_2)}} \quad (11)$$

where, $X_1$ and $X_2$ are two spectral vectors. 'Cov' stands for covariance computation, 'Var' stands for variance computation. The value of r represents for the similarity of two spectra.

## RESULTS AND DISCUSSION

**Transfer on the FT Raman spectrometer:** Samples benzene and cyclohexane were measured on MultiRAM at nominal resolutions 1, 2, 4, 8, 12 $cm^{-1}$ all 64 times with 500 mW laser power. Fig. 2 shows all the cyclohexane Raman spectra for comparison. The influence of the resolution parameter on Raman spectra could be seen from the enlarged band in the figure.

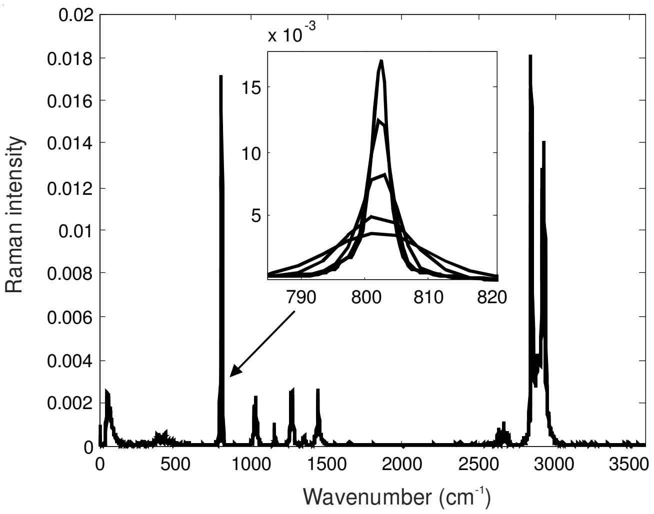

Fig. 2. Cyclohexane Raman spectra measured by the MultiRAM spectrometer with five different resolutions (1, 2, 4, 8, 12 $cm^{-1}$). The peak at position around 800 $cm^{-1}$ was enlarged for a clear comparison

These Raman spectra with high resolutions were transferred to low resolutions using our algorithm. Before resolution transfer, each spectrum was interpolated to 3600-200 cm$^{-1}$ Raman shift region with 0.5 cm$^{-1}$ interval, then preprocessed with a maximum normalization. After convolution, the spectrum was maximum normalized too.

As the resolution is a preset parameter for FT-Raman spectrometer, the Gaussian transfer function can be easily formed with eqn. (10). Fig. 3 shows the result of benzene and cyclohexane spectra transferred from resolution 1 cm$^{-1}$ to 8 cm$^{-1}$. From Fig. 3, more and narrower peaks could be obtained with a high resolution, while weak peaks would be submerged by nearby strong peaks when resolution reduces. After resolution transfer, peaks are widened and overlapped and the transferred spectra are almost consistent with the measured spectra. Another view of the result is the improvement of the correlation coefficients after resolution transfer. 6 Sets of transfer from a high resolution to a low resolution were processed and comparative results are listed in Table-1. Even from resolution 1 cm$^{-1}$ to 12 cm$^{-1}$ (the highest to the lowest), the correlation coefficient (r) can reach 0.99 after transfer.

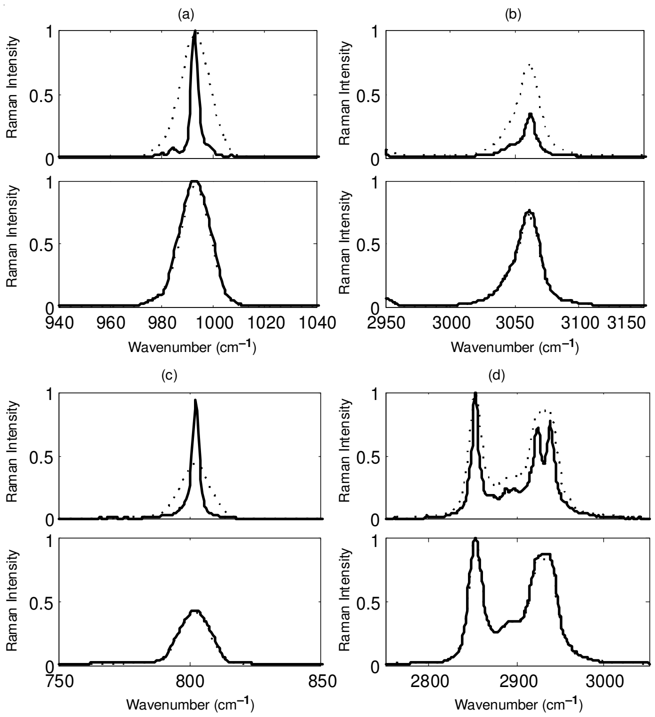

Fig. 3. Transfer of benzene and cyclohexane Raman spectra from resolution 1 cm$^{-1}$ to 8 cm$^{-1}$ on MultiRAM. Subfigures (a), (b) show two bands of benzene and (c), (d) show two bands of cyclohexane. At top of each subfigure, the continuous lines are measured spectra with resolution 1 cm$^{-1}$, the dashed lines are measured spectra with resolution 8 cm$^{-1}$. At bottom, the continuous lines are spectra transferred from resolution 1 cm$^{-1}$ to 8 cm$^{-1}$, the dashed lines are measured spectra with resolution 8 cm$^{-1}$

**Transfer between two dispersive CCD spectrometers:** The samples benzene, cyclohexane and *m*-xylene were measured on BTC162E and QE65000 respectively under the identical circumstance. Before applying convolution for spectra transfer, wavelength/wavenumber positions along the abscissa and relative intensities along the ordinate should both be corrected for accurate Raman spectral analysis.

TABLE-1
COMPARISON OF CORRELATION COEFFICIENTS (r) BETWEEN SOURCE AND TARGET SPECTRA BEFORE AND AFTER RESOLUTION TRANSFER ON MULTIRAM

| | Benzene | | Cyclohexane | |
|---|---|---|---|---|
| | Before | After | Before | After |
| 1 cm$^{-1}$ to 4 cm$^{-1}$ | 0.93187 | 0.99834 | 0.98628 | 0.99795 |
| 1 cm$^{-1}$ to 8 cm$^{-1}$ | 0.83342 | 0.99879 | 0.95650 | 0.99780 |
| 1 cm$^{-1}$ to 12 cm$^{-1}$ | 0.75875 | 0.98762 | 0.93135 | 0.98931 |
| 2 cm$^{-1}$ to 8 cm$^{-1}$ | 0.88347 | 0.99898 | 0.96869 | 0.99847 |
| 2 cm$^{-1}$ to 12 cm$^{-1}$ | 0.77334 | 0.98751 | 0.94485 | 0.99119 |
| 4 cm$^{-1}$ to 12 cm$^{-1}$ | 0.90665 | 0.99485 | 0.96836 | 0.99564 |

Some simple techniques have been employed to calibrate the wavenumber of a dispersive Raman spectrometer[19-27]. Atomic line sources, *e.g.*, argon and neon lamps, are more preferred in practice[22,23]. This approach is to fit a polynomial to a small number of reference line positions that are emitted by the light sources. Argon lamps providing sharp emission lines in NIR region are readily introduced to a Raman system using 785 nm laser. An AR-1 Argon light source from Ocean Optics, Inc. was adopted for wavenumber calibration in our work.

Wavenumber positions of both BTC162E and QE65000 were corrected. Fig. 4. shows the result of wavenumber calibration with two peaks from benzene and cyclohexane. After this step of calibration, the spectra from two instruments were interpolated into 200-2000 cm$^{-1}$ wavenumber range with 1 cm$^{-1}$ interval.

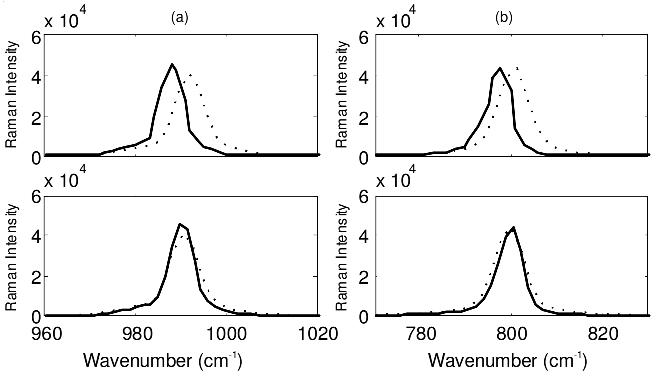

Fig. 4. Wavenumber calibration for BTC162E (continuous line) and QE65000 (dashed line). (a) 990 cm$^{-1}$ benzene Raman peak, (b) 800 cm$^{-1}$ cyclohexane Raman peak. Curves at top were plotted with original wavenumber read out from the spectrometer software, while at bottom with calibrated wavenumber

Inferior to absorbance spectroscopy, Raman spectroscopy is a single-beam technique without internal response calibration. Raman spectral response obtained with different dispersive instruments may vary significantly in intensity, due to their wavelength-dependent optical transmission, quantum efficiency of detector elements and pixel-to-pixel variation in CCD detector. The intensity variation must be eliminated with some standards before applying convolution. Normally, intensity correction of Raman spectroscopy deals with the relative response across the instrument spectral range, rather than its absolute response. Sample composition is determined from band ratios of Raman spectra, rather than the absolute response in absorbance measurements[24,25].

Second emission standards that produce stable fluorescence with laser irradiation are preferred for routine laboratorial calibration[26,27]. They are convenient to use without additional equipments and need no periodical recalibration. Standard reference material SRM 2241 is certified by NIST as a relative intensity standard for Raman spectra obtained with laser exciting at 785nm wavelength[28]. SRM 2241 is a luminescent glass with good photo stability and its temperature impact can be ignored in the laboratory environment. The spectrum of SRM 2241 on a standard spectrometer was suggested to be calculated by a fifth-order polynomial. The procedure for relative intensity correction requires to measure the luminescence spectra of the SRM and to calculate the correction coefficients for each spectral pixel.

Fig. 5 shows three shapes of luminescence spectra by SRM 2241: one standard spectrum calculated from the fifth-order polynomial and two measured spectra obtained with BTC162E and QE65000. The nonlinear effect of different CCD detectors can be observed obviously in Fig. 5, which makes relative intensity correction indispensable. The response curve of BTC162E seems to be a parabola, while that of QE65000 mimics the standard curve but with up-and-down waves.

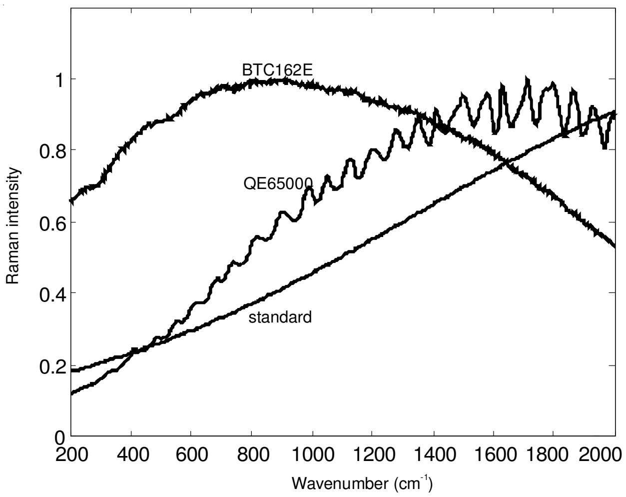

Fig. 5. Comparison of standard and measured luminescence spectra by SRM 2241. The intensity of each measured spectrum was maximum normalized to be compared with standard spectra

Fig. 6 shows the result of relative intensity correction for cyclohexane spectra. The normalized intensities of the peaks at positions between 1500-1000 $cm^{-1}$ have much difference, which were largely decreased after correction.

After wavenumber calibration for both spectrometers and relative intensity correction for each Raman spectra, the convolution procedure could be applied to transfer the spectra. As stated above in the theory section, the resolution parameter of both source and target instruments should be acquired to build the Gaussian transfer function. Indeed, atomic lamps are not only used as wavenumber calibration references, but also good sources for resolution testing. Because the sharp emission lines are pure Gaussian which is the result of the instrument. The AR-1 argon light source was utilized again to test the resolution of BTC162E and QE65000.

Fig. 7 shows the argon line around 1005 $cm^{-1}$, which is to estimate the resolution from the curve. The full-width at half-height of both spectrometers were indicated with "↔" on the curves. We can learn that the resolution of BTC162E (2.43 $cm^{-1}$) is almost 2 times higher than that of QE65000 (4.97 $cm^{-1}$). Then, the full-width at half-height are converted to the Gaussian widths with eqn. (5) to build the Gaussian transfer function with eqn. (11). And the Gaussian transfer function was discretized with the same step to interpolate the spectra.

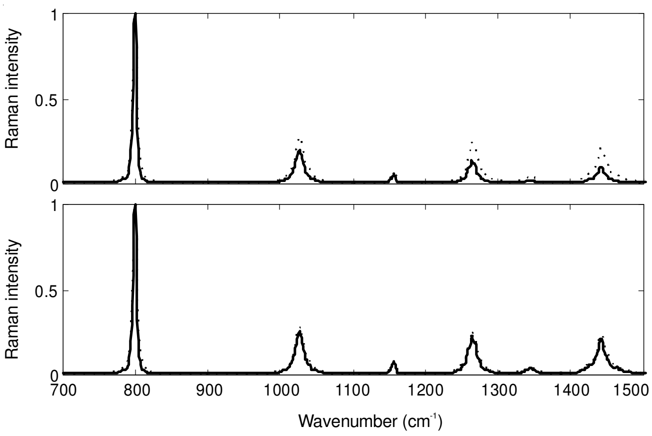

Fig. 6. Relative intensity correction for cyclohexane spectra by BTC162E (continuous line) and QE65000 (dashed line). Curves at top were uncorrected, while at bottom were corrected using SRM 2241

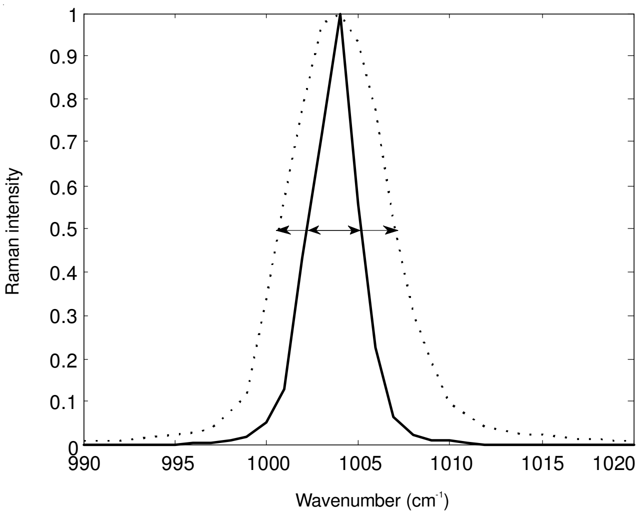

Fig. 7. Normalized argon lines around 1005 $cm^{-1}$ to test resolution of BTC162E (continuous line) and QE65000 (dashed line)

Raman spectra of benzene, cyclohexane and *m*-xylene were transferred from BTC162E to QE65000 applying convolution with the Gaussian transfer function. After that, the spectrum is maximum normalized to correct the overall intensity. Fig. 8 shows the transfer result with two peaks from benzene and cyclohexane. The slight variation in peak width is decreased after convolution. Table-2 shows the improvement of the correlation coefficients by wavenumber calibration, relative intensity correction and transfer procedure. The method combining our transfer procedure with established correction procedures makes good effects in transfer of Raman spectra measured on different spectrometers. It seems that wavenumber calibration or relative intensity correction contributes more than resolution transfer. That's because the resolution gap between the two spectrometers in experiment is not large, so the main difference has been corrected before convolution.

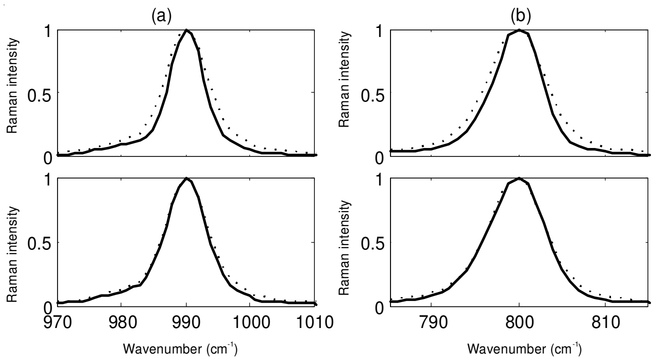

Fig. 8. Spectra transfer from BTC162E (continuous line) to QE65000 (dashed line) applying convolution. (a) 990 cm$^{-1}$ benzene Raman peak, (b) 800 cm$^{-1}$ cyclohexane Raman peak. The continuous lines were measured spectra by QE65000. The dashed lines at top were measured spectra by BTC162E, while at bottom were transferred from BTC162E to QE65000

TABLE-2
IMPROVEMENTS OF THE CORRELATION COEFFICIENTS ($r$) OF SPECTRA BETWEEN BTC162E AND QE65000 BY WAVENUMBER CALIBRATION, RELATIVE INTENSITY CORRECTION AND TRANSFER PROCEDURE

| | Original | After wavenumber calibration | After relative intensity correction | After resolution transfer |
|---|---|---|---|---|
| Benzene | 0.70580 | 0.98455 | 0.98510 | 0.99742 |
| Cyclohexane | 0.75677 | 0.96821 | 0.99065 | 0.99760 |
| *m*-Xylene | 0.75184 | 0.94373 | 0.98588 | 0.99665 |

## Conclusion

This paper presents a procedure for transfer of Raman spectra from relatively higher to lower resolution. Unlike traditional calibration transfer methods based on chemometrics, a set of standard samples is not needed to be prepared and measured on both the source and target instruments. The only thing required is to convolute the spectra with a Gaussian transfer function, which has been certified with Raman spectral model built by Voigt function. Given the resolution of both spectrometers (or measurement environments), the transfer function could be easily established. It saves great time and effort, comparing to previous transfer methods.

The effectiveness of the convolution procedure has been checked by transferring spectra between different resolutions on a FT-Raman spectrometer. Furthermore, with the addition of procedures for wavenumber calibration and relative intensity correction, spectra transfer was successfully preformed between different dispersive CCD Raman spectrometers. The results suggest that this method should be applicable to all kinds of applications for Raman spectra calibration transfer.

## ACKNOWLEDGEMENTS

This work was supported by the National High Technology Research and Development Program ("863" Program) of China Grant No. 2009AA04Z123.

## REFERENCES

1. E. Smith and G. Dent, Modern Raman Spectroscopy-A Practical Approach, John Wiley & Sons, Chichester (2005).
2. M. Kompany-Zareh and F. van den Berg, *Analyst*, **135**, 1382 (2010).
3. R.N. Feudale, N.A. Woody, H. Tan, A.J. Myles, S.D. Brown and J. Ferre, *Chemom. Intell. Lab. Syst.*, **64**, 181 (2002).
4. F. Despagne, D.L. Massart, M. Jansen and H. van Daalen, *Anal. Chim. Acta*, **406**, 233 (2000).
5. F.A. Honorato, R.K.H. Galvao, M.F. Pimentel, B. de Barros Neto, M.C.U. Araujo and F. Rodrigues de Carvalho, *Chemom. Intell. Lab. Syst.*, **76**, 65 (2005).
6. D. Ozdemir, M. Mosley and R. Williams, *Appl. Spectrosc.*, **52**, 599 (1998).
7. Y. Wang and B.R. Kowalski, *Appl. Spectrosc.*, **46**, 764 (1992).
8. C.F. Pereiraa, M.F. Pimentela, R.K.H. Galvao, F.A. Honoratoa, L. Stragevitcha and M.N. Martins, *Anal. Chim. Acta*, **611**, 41 (2008).
9. C.M. Gryniewicz-Ruzicka, S. Arzhantsev, L.N. Pelster, B.J. Westenberger, L.F. Buhse and J.F. Kauffman, *Appl. Spectrosc.*, **65**, 334 (2011).
10. Y. Wang, D.J. Veltkamp and B.R. Kowalski, *Anal. Chem.*, **63**, 2750 (1991).
11. J.S. Shenk and M.O. Westerhaus, US Patent 4866644 (1989).
12. H.N. Quang, M. Jouan and N.Q. Dao, *Anal. Chim. Acta*, **379**, 159 (1999).
13. C.K. Mann and T.J. Vickers, *Appl. Spectrosc.*, **53**, 856 (1999).
14. R.J. Meier, *Vib. Spectrosc.*, **39**, 266 (2005).
15. J.D. Ingle and S.R. Crouch, Spectrochemical Analysis. Prentice-Hall, New Jersey (1988).
16. H.O. Di Rocco, D.I. Iriarte and J. Pomarico, *Appl. Spectrosc.*, **61**, 117 (2007).
17. S.D. Bruce, J. Higinbotham, I. Marshall and P.H. Beswick, *J. Magn. Reson.*, **142**, 57 (2000).
18. B.T. Bowie and P.R. Griffiths, *Appl. Spectrosc.*, **57**, 190 (2003).
19. D.A. Carter and J.E. Pemberton, *Appl. Spectrosc.*, **49**, 1550 (1995).
20. D.A. Carter, W.R. Thompson, C.E. Taylor and J.E. Pemberton, *Appl. Spectrosc.*, **49**, 1561 (1995).
21. A.W. Fountain III, T.J. Vickers and C.K. Mann, *Appl. Spectrosc.*, **52**, 462 (1998).
22. C. Tseng, J.F. Ford, C.K. Mann and T.J. Vickers, *Appl. Spectrosc.*, **47**, 1808 (1993).
23. T.J. Vickers and C.K. Mann, *Appl. Spectrosc.*, **53**, 1617 (1999).
24. J.M. Tedesco and K.L. Davis, Proceedings of the Society of Photo-optical Instrumentation Engineers (SPIE), **3537**, 200 (1999).
25. J.R. Beattie, J.V. Glenn, M.E. Boulton, A.W. Stitt and J.J. McGarvey, *J. Raman Spectrosc.*, **40**, 429 (2009).
26. J.A. Gardecki and M. Maroncelli, *Appl. Spectrosc.*, **52**, 1179 (1998).
27. K.J. Frost and R.L. McCreery, *Appl. Spectrosc.*, **52**, 1614 (1998).
28. S.J. Choquette, E.S. Etz, W.S. Hurst, D.H. Blackburn and S.D. Leigh, *Appl. Spectrosc.*, **55**, 822 (2001).