

Entropy minimization and spectral dissimilarity curve resolution technique applied to nuclear magnetic resonance data sets

Effendi Widjaja, Marc Garland*

Department of Chemical and Biomolecular Engineering, 4 Engineering Drive 4, National University of Singapore 117576, Singapore

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Abstract

The use of entropy minimization and spectral dissimilarity is applied to three nuclear magnetic resonance (NMR) data sets. The data sets contain 2, 2, and 3 observables each. It was found that without any a priori information the sets of pure component spectra underlying the NMR spectroscopic observations could be extracted. These successful spectral resolutions suggest that a combined entropy minimization and spectral dissimilarity approach can be further developed for even larger NMR data sets containing a larger number of observables. Brief comparison to DECRA and PMF curve resolution results is also presented.

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1. Introduction

Various methods to process diffusion ordered NMR data have been developed so far, such as Levenberg–Marquadt (L–M), DISCRETE, SPLMOD, CONTIN, and maximum entropy method (MaxEnt) [1,2], with the main goal to transform NMR data sets, which are stack plots of attenuated spectra, into 2D spectra with chemical shifts on one axis and the distribution of diffusion coefficients on the other. However, when there is severe overlap of NMR peaks, these methods are usually not good alternatives. Multivariate data of the analysis, such as the popular self-modeling curve resolution (SMCR) methods can overcome this limitation, since the goal of SMCR is to isolate the NMR peaks for each individual species.

In recent years, the usefulness of SMCR methods to analyze spectroscopic data has become widely recognized. With the aid of SMCR, it is possible to eliminate the tedious separation of multi-component mixtures before some or even all the unknown components can be

identified and characterized. Based on the mixture spectral data alone, one can determine the number of underlying components, extract their pure component spectral information, and obtain relative concentration profiles.

Various SMCR methods have been suggested in the past few years to elucidate NMR data. These include the applications of multivariate curve resolution based on alternating least-squares optimisation (MCR-ALS) [3,4], direct exponential curve resolution algorithm (DECRA) [5], positive matrix factorisation (PMF) [6], non-iterative methods based on principal component analysis (EFA, WFA, and HELP) and a constrained key variable regression (CKVR) [7], and Simplisma [8]. SMCR methods are sometimes also referred to as complete band shape methods in the NMR literature [1]. However, until now, information entropy minimization concepts have not been applied to NMR data to recover pure component spectra, although such concepts have been applied for NMR phase-correction [9]. Thus, in this paper, this approach is described and its applicability to NMR data is investigated.

The concept of Shannon's information entropy can be defined as a measure of choice and uncertainty

* Corresponding author. Fax: +65 6779 1936.

E-mail address: chemvg@nus.edu.sg (M. Garland).

[10], in which uncertainty means the random and disorder information. A clearer definition of entropy was later given by Weaver, Shannon's collaborator. He defined it as: "in the physical sciences, the entropy associated with a situation is a measure of the degree of randomness or of "shuffled-ness" if you will, in the situation; and the tendency of physical systems to become less and less organized, to become more and more perfectly shuffled. . ." [11]. Therefore by this definition, lowering information entropy will generate the reverse effects, and a more organized and simpler system is obtained. In application to curve resolution, it is assumed that the recovered pure component spectra have the least entropy compared to the experimental mixture spectra. The recovered pure component spectrum will have simpler and less line shape and thus, it has smaller entropy value. In other words, minimizing entropy localizes the spectral information around the major bands and maximizes the number of zero elements in the recovered spectrum.

The application of entropy minimization approach to resolve pure component spectra was initiated by Sasaki et al. [12,13]. Later, this approach was employed by Brown and Harper [14] to resolve mass spectroscopic data. Zeng and Garland [15] successfully revised Sasaki's model to allow curve resolutions from mixtures consisting of highly overlapping spectral features. It was found that a fourth order derivative instead of a second order derivative of the estimated absorptivity facilitated better spectral resolution. Also, Pan et al. [16] applied various entropy minimization models to piecewise continuous infrared spectral data from a two-component mixture of organometallics having highly overlapping spectral features.

However, when entropy minimization alone was employed to resolve large-scale multi-component systems with extremely overlapping spectral features, there was a tendency for the algorithms to generate repetitive spectral patterns. Additional functions or constraints are therefore needed to obtain proper resolution. Effendi and Garland [17] proposed some objective functions that combine the use of entropy minimization and spectral dissimilarity to overcome this problem. It was successfully applied to a synthetic seven-species data set. Later, Chen et al. [18] also successfully applied a similar approach to recover pure component spectra from in situ FTIR reaction spectral data, which were collected from a series of homogeneous rhodium catalyzed hydroformylations of isoprene.

Three different pulsed gradient spin echo (PGSE) nuclear magnetic resonance (NMR) data sets whose concentrations profiles decay exponentially were used as standard data sets [19]. Windig and Antalek [5] conducted the experiments and applied one of the variations of generalized rank annihilation method (GRAM) namely direct exponential curve resolution (DECRA)

to directly resolve the mixture data. The DECRA approach gave a unique curve resolution solution and could be executed in a very short time. However, its analysis demands the compounds having exponentially concentration profiles.

Xie et al. [6] re-investigated these three NMR spectral data sets using a least square approach namely positive matrix factorization (PMF) to elucidate the pure component spectra. Their investigation showed that PMF could solve the analytical curve resolution problems. The qualities of the spectral estimates were comparable and consistent with those obtained from the DECRA approach. No further reconstruction quality improvement was obtained.

In the present contribution, an information entropy approach similar to that previously used to analyze FTIR spectral data is now employed to PGSE-NMR data. Instead of using an inner product between spectra, we use determinants of the covariance matrix to calculate the degree of spectral dissimilarity. Good pure-component spectral recovery is obtained. The spectral resolution results are briefly compared to those obtained using DECRA [5] and PMF [6] techniques.

2. Computational aspects

In principle, this technique works through a combination of singular value decomposition (SVD) [20], entropy minimization, spectral dissimilarity, and simulated annealing approaches. It starts with data matrix decomposition by SVD, followed by rotation of the resulting basis vectors into physically meaningful pure component spectra:

$$\mathbf{D}_{k \times v} = \mathbf{C}_{k \times s} \mathbf{a}_{s \times v} + \varepsilon_{k \times v}. \quad (1)$$

$\mathbf{D}_{k \times v}$ represents an experimentally measured spectral data matrix, where k denotes the number of spectra and v is the number of data channels or number of variables (e.g., wavenumber, ppm, Raman shift). The $\mathbf{D}_{k \times v}$ matrix arises from the product of a concentration matrix $\mathbf{C}_{k \times s}$ and the pure component spectra matrix $\mathbf{a}_{s \times v}$, and $\varepsilon_{k \times v}$ is the experimental error matrix, where s denotes number of observable species in chemical mixture.

$$\mathbf{D}_{k \times v} = \mathbf{U}_{k \times k} \mathbf{\Sigma}_{k \times v} \mathbf{V}_{v \times v}^T, \quad (2)$$

$$\hat{\mathbf{D}}_{k \times v} \approx \hat{\mathbf{C}}_{k \times s} \hat{\mathbf{a}}_{s \times v} = \mathbf{U}_{k \times s} \mathbf{\Sigma}_{s \times z} \mathbf{T}_{s \times z}^{-1} \mathbf{T}_{s \times z} \mathbf{V}_{z \times v}^T, \quad k \geq z \geq s, \quad (3)$$

$$\hat{\mathbf{C}}_{k \times s} = \mathbf{U}_{k \times s} \mathbf{\Sigma}_{s \times z} \mathbf{T}_{s \times z}^{-1} = \mathbf{D}_{k \times v} \hat{\mathbf{a}}_{v \times s}^T (\hat{\mathbf{a}}_{s \times v} \hat{\mathbf{a}}_{v \times s}^T)^{-1}. \quad (4)$$

The consolidated data matrix $\mathbf{D}_{k \times v}$ is then subjected to SVD Eq. (2), to obtain its abstract orthonormal left and right singular matrices $\mathbf{U}_{k \times k}$ and $\mathbf{V}_{v \times v}^T$ and its singular

matrix $\Sigma_{k \times v}$. Furthermore, $\mathbf{D}_{k \times v}$ can be approximated by Eq. (3), where z is the number of right singular vectors used for spectral reconstruction/transformation. $\mathbf{T}_{s \times z}$ is a rectangular transformation matrix that maps the vector-space of $\mathbf{V}_{z \times v}^T$ into $\hat{\mathbf{a}}_{s \times v}$, the matrix of averaged pure component spectral estimates for the s species. $\mathbf{T}_{s \times z}^{-1}$ is then a generalized inverse and $\hat{\mathbf{C}}_{k \times s}$ is the corresponding expectation for concentrations calculated from Eq. (4).

$$\hat{\mathbf{a}}_{s \times v} = \mathbf{T}_{s \times z} \mathbf{V}_{z \times v}^T. \quad (5)$$

The transformation of the z right singular vectors into a set of pure component spectral estimates (Eq. (5)) is associated with the global optimization of the $s \times z$ elements in the \mathbf{T} matrix, based on the proposed non-linear constrained objective function. This objective function includes the non-negative solutions of estimated pure component spectra $\hat{\mathbf{a}}_{s \times v}$ as well as the corresponding concentrations $\hat{\mathbf{C}}_{k \times s}$, an entropy function, and a spectral dissimilarity function.

2.1. Non-negative solutions

$$P(\hat{\mathbf{a}}_{s \times v}, \hat{\mathbf{C}}_{k \times s}) = \gamma_a F_1(\hat{\mathbf{a}}_v) + \gamma_c F_2(\hat{\mathbf{C}}_k), \quad (6)$$

where

$$F_1(\hat{\mathbf{a}}_v) = \sum_v (\hat{\mathbf{a}}_v)^2 \forall \hat{\mathbf{a}}_v < 0, \quad (7)$$

$$F_2(\hat{\mathbf{C}}_k) = \sum_k (\hat{\mathbf{C}}_k)^2 \forall \hat{\mathbf{C}}_k < 0, \quad (8)$$

$$\gamma_a = \begin{cases} 0 & F_1(\hat{\mathbf{a}}_v) < \lambda_1, \\ 10 & \lambda_1 \leq F_1(\hat{\mathbf{a}}_v) < \lambda_2, \\ 10^4 & F_1(\hat{\mathbf{a}}_v) \geq \lambda_2, \end{cases} \quad (9)$$

$$\gamma_c = 10^3 \forall F_2(\hat{\mathbf{C}}_k). \quad (10)$$

All admissible estimates for the pure component spectra must ensure non-negativity in the estimated $\hat{\mathbf{a}}_{s \times v}$ as well as the associated concentrations $\hat{\mathbf{C}}_{k \times s}$. However, soft non-negativity constraints are imposed, in which slightly negative estimates are still acceptable. γ_a and γ_c are penalty coefficients for the constraints defined by Eqs. (9) and (10), and $\lambda_1 = 10^{-3}$ and $\lambda_2 = 10^{-2}$ are bounds for the pure-component spectra-estimate constraints defined in Eq. (9).

2.2. Entropy function

$$H = - \sum_s \sum_v h_{sv} \ln(h_{sv}). \quad (11)$$

To measure the degree of spectral simplicity, a Shannon [21] type information entropy function was employed.

$$h_{sv} = \frac{|\hat{a}_{sv}^m|}{\sum_v |\hat{a}_{sv}^m|}. \quad (12)$$

The measure H is the information entropy, and h_{sv} is a discrete probability distribution function that can be defined as the absolute value of the derivative of the estimated spectrum in an L^1 norm.

The exponent m is the degree of spectral differentiation, either first derivative, second derivative or fourth derivative. The degree of differentiation will depend on the noise level of the mixture spectra acquired. Higher derivatives may be employed if the signal to noise ratio (S/N) of mixture spectrum is high. However, if noise intensity is quite high (S/N is low), it is preferable to use a lower degree of differentiation.

2.3. Dissimilarity function

Spectral dissimilarity can be quantified as a distance measure involving the pure component spectral estimates. Since it can be assumed that each pure component should have its own distinct or unique pure spectrum, maximizing the dissimilarities among the reconstructed pure component spectra can be useful—however, over-resolution may also occur. A distance measure is employed to prevent identical spectral reconstructions from occurring since s spectra are resolved simultaneously.

$$\varsigma_a = |\hat{\mathbf{a}}_{s \times v} \hat{\mathbf{a}}_{v \times s}^T|. \quad (13)$$

In the current study, the distance measure is represented by a determinant of the covariance matrix of L^2 norm resolved spectral estimates $\hat{\mathbf{a}}_{s \times v}$.

2.4. Objective function

$$\text{Min } F_{\text{obj}} = H + P - \lambda \varsigma_a \text{ w.r.t. } T_{s \times z}. \quad (14)$$

The above non-negativity, signal entropy, and dissimilarity criteria form the basis for the general objective function used in the current study, where λ is the weightage for the determinant of the covariance matrix. The purpose of a weightage is to balance the magnitudes of the entropy function and determinant values.

The final estimate of $\hat{\mathbf{a}}_{s \times v}$, corresponds to the global minimum value of the proposed objective function. This is performed by a global optimization method, specifically Corana's Simulated Annealing [22]. It is widely accepted that Corana's SA is a reliable tool for finding globally optimal solutions.

In brief, it should be highlighted that the data analysis execution is simple. All parameters in this optimization are fixed, except the number of components, s , and the number of eigenvectors, z , to be rotated, which are the open variables. The algorithm took only a few minutes with the present data set, and easily converged from the initial right singular vectors to the final recovered spectra. Some limitations of the present algorithm

for very large values of s have been mentioned before [17,18].

3. Experiments

Three sets of samples were analyzed from the ^1H PGSE-NMR experiments [19], and full details of the experimental method can be found in [5]. Briefly, the first set was a mixture of 0.1% w/w TX-100 (a non-ionic surfactant) in water, and 5% w/w gelatine in water. In this experiment, 20 mixture spectra were measured with 4095 data points each (range -0.58 to 8.1 ppm). The second set was a mixture of 0.15% w/w di-(C6-Glu) in water which is also a non-ionic surfactant, and 5% w/w gelatine in water. Again 20 mixture spectra were taken with 4095 data points each (range -0.58 to 8.1 ppm). The third sample was a mixture of two components, 2-chloropropionic acid 0.94% w/w and 2-aminobenzothiazole 1.2% w/w, in dimethyl sulfoxide- d_6 (DMSO). In this experiment, 15 spectra were recorded with 6218 points each (range 0.49 – 8.24).

However, not all measured data were used for spectral reconstruction. According to Windig and Antalek, the first spectrum and/or a few spectra were excluded in the data analysis because these spectra were only from water resonance or they deviated substantially from the other spectra. Therefore, only spectra 2–13, spectra 2–11, and spectra 2–15 were used for mixtures 1–3, respectively.

4. Results and discussion

Because the signal-to-noise ratio of these three data sets was quite low, the spectral resolution of mixture spectra was performed using a low derivative entropy measure, namely a first derivative measure.

4.1. Mixture gelatin and TX-100

The 12-mixture spectra were consolidated and were decomposed by SVD. Fig. 1 shows the spectra 2–13 and Fig. 2 shows the first four \mathbf{V}^T vectors. It is visually very clear that only the first two \mathbf{V}^T vectors are physically important and have meaningful information. Nevertheless, we also performed an F test on the generated singular values, and it predicts only two observable components. Beyond the second vector, all vectors appear to consist almost entirely of white noise. Thus for rotation, only the first 2 vectors were subject to an entropy-minimized objective function. In addition, the DECRA approach to resolve pure component spectra was also used. The DECRA MATLAB function was obtained together with the downloadable PGSE-NMR spectral data sets.

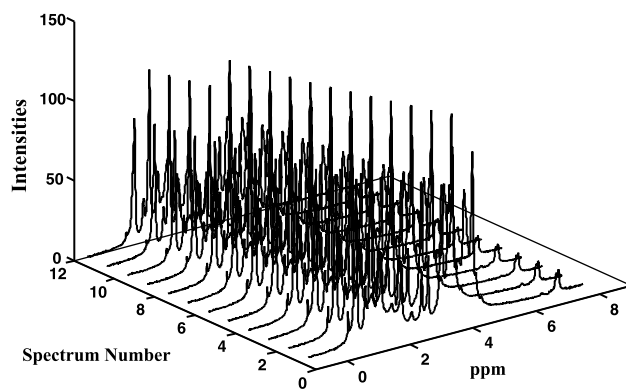


Fig. 1. Experimental mixture spectra (2–13) of the gelatin and TX-100. This data set is available in [19]. These mixture spectra are the only information we have about the mixture components and are the basis for curve resolution.

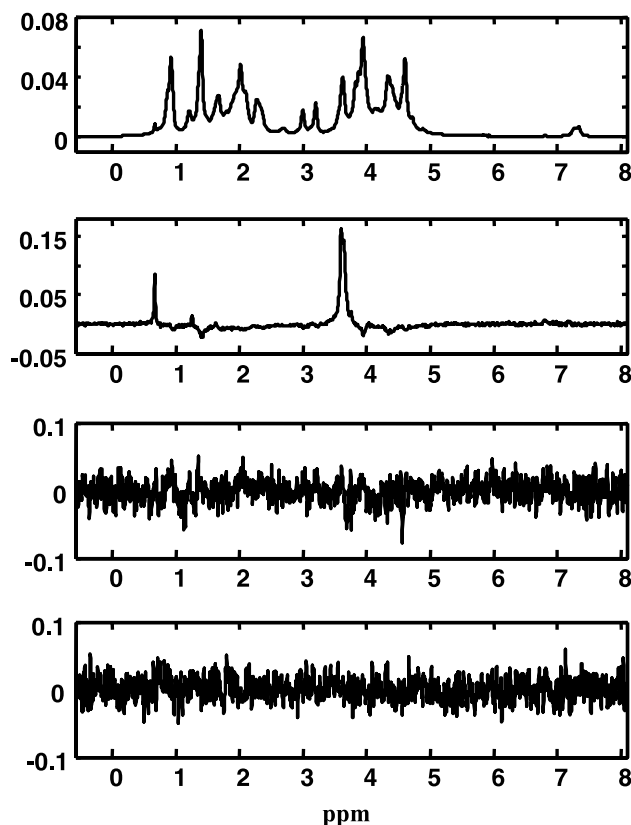


Fig. 2. The first four right singular vectors of the gelatin and TX-100 mixture data.

The reference spectra, the spectral estimates obtained via entropy minimization and the DECRA results are presented in Fig. 3. It is seen that the spectral estimates of gelatin and TX-100 were well resolved through the entropy-minimized approach.

Since mixture spectra are formed from a bilinear structure as described in Eq. (1), relative concentrations of gelatin and TX-100 could be calculated directly using a pseudo inverse approach, and their profiles are shown

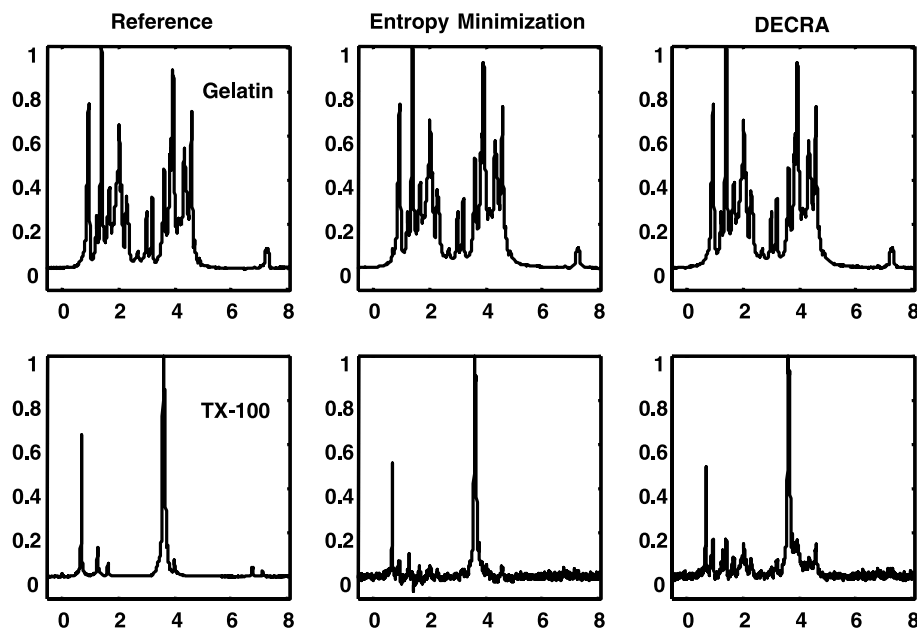


Fig. 3. Pure component spectra of gelatin and TX-100 obtained from experimental references and curve resolution via entropy minimization and DECRA (ordinate: normalized intensity; abscissa: ppm).

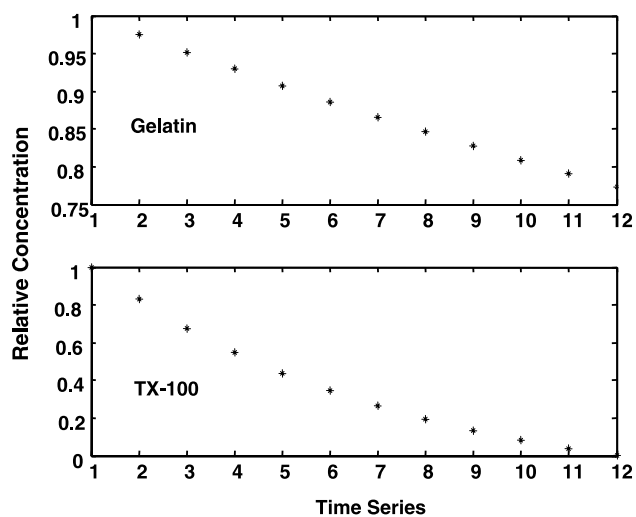


Fig. 4. Relative concentration profiles of gelatin and TX-100 in time series.

in Fig. 4. The relative concentrations of these two compounds decay exponentially in time.

4.2. Mixture gelatin and di-(C6 Glu)

Similar to the previous data set, 11 mixture spectra were consolidated and decomposed using SVD. As only the first 2 V^T vectors were significant, these two vectors accordingly were transformed into two pure spectral estimates. The reference spectra, spectral estimates obtained via entropy minimization and DECRA were presented in Fig. 5. Although, both the entropy minimization and DECRA methods provide rather

good spectral estimates of the gelatin, lower quality estimates of di-(C6 Glu) are obtained. It was obvious from the reference spectra that these two components were severely overlapped. However, clear identification still can be observed.

4.3. Mixture of 2-aminobenzothiozole and 2-chloropropionic acid in DMSO

This spectral data set was actually a four component system involving DMSO solvent and water. However, after consolidation of these 14 mixture-spectra and data decomposition through SVD, the V^T matrix revealed that only the first 3 V^T vectors contain real signal information. The fourth V^T vector and beyond only consisted of noise signals. As noted elsewhere, this problem suggested that the current system was rank-deficient since its data matrix rank was apparently lower than number of components [5]. Thus, only three vectors were taken and square rotation entropy minimization was imposed. The spectral estimates obtained via entropy minimization and DECRA are presented in Fig. 6.

The first spectral estimate shows a superposition of DMSO and water pure component spectra. Such an estimate indicates that there is a collinearity problem. In addition, none of the estimates appear to be very pure. This suggests that there was a better experimental design would have been useful. Since the reference pure component spectra were not provided for these compounds, a quantitative evaluation of spectral estimates could not be performed. However, Fig. 6 shows that similar reconstruction results were obtained from DECRA and entropy minimization.

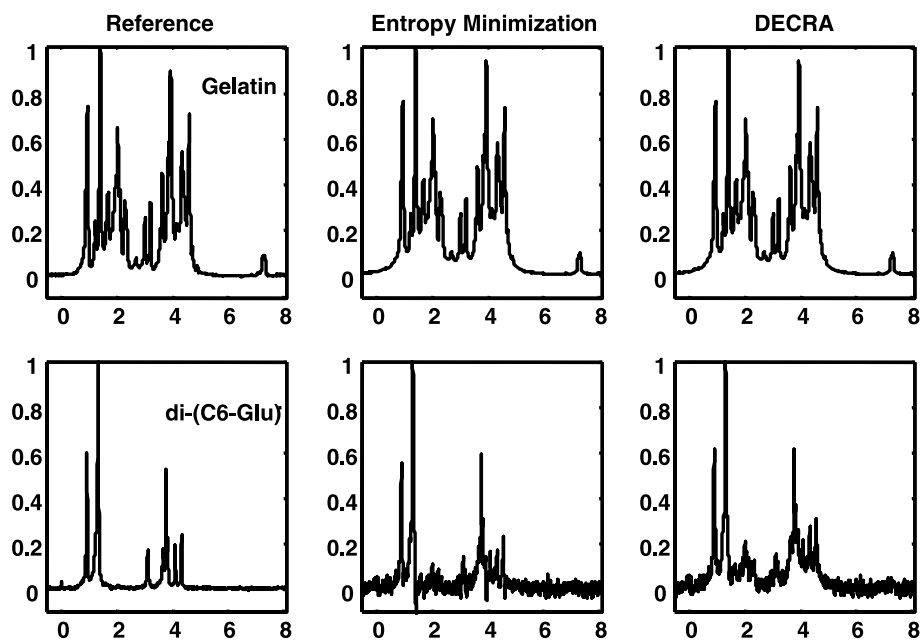


Fig. 5. Pure component spectra of gelatin and di-(C6-Glu) obtained from experimental references and curve resolution via entropy minimization and DECRA (ordinate: normalized intensity; abscissa: ppm).

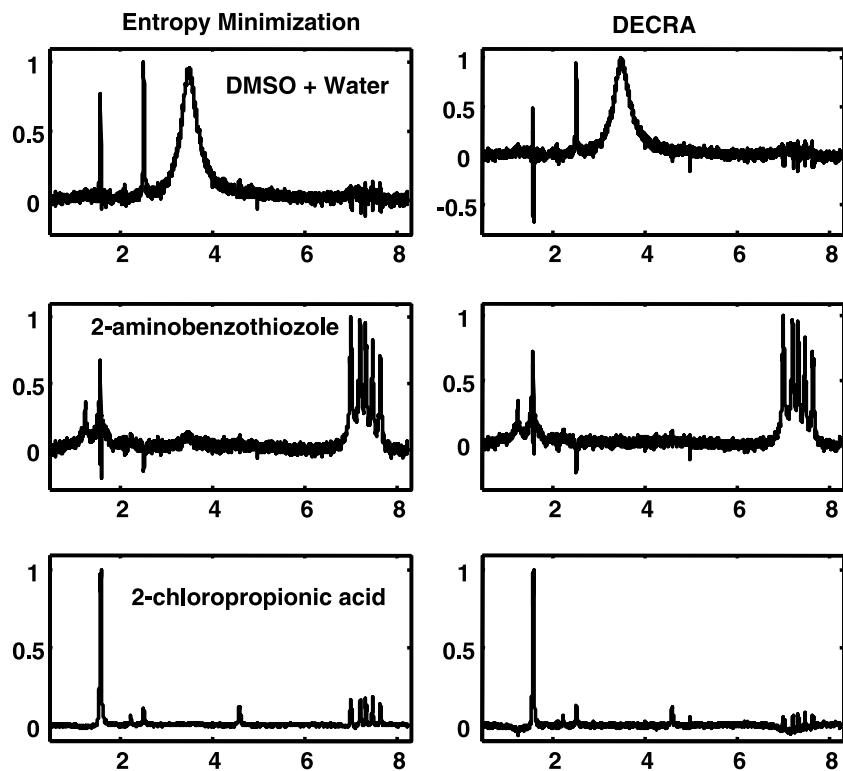


Fig. 6. Pure component spectral estimates of DMSO + water, 2-aminobenzothiozole, and 2-chloropropionic acid obtained via entropy minimization and DECRA (ordinate: normalized intensity; abscissa: ppm).

4.4. Comparison study of entropy minimization, DECRA, and PMF curve resolution results

From the previous three spectral reconstruction results, it is clear that the entropy minimization technique

is useful for ^1H PGSE-NMR mixture spectra. Moreover, since the reference spectra of the first two data sets are provided, the resolution quality of each curve resolution technique can be computed and compared. Correlation coefficients were used to compare the resolved and

Table 1
Correlation coefficients for the mixture gelatin and TX-100 obtained via DECRA, PMF, and entropy methods

Component	DECRA	PMF	Entropy
Gelatin	0.995	0.995	0.995
TX-100	0.930	0.930	0.973

Table 2
Correlation coefficients for the mixture gelatin and di-(C6 Glu) Obtained via DECRA, PMF, and entropy methods

Component	DECRA	PMF	Entropy
Gelatin	0.993	0.993	0.993
di-(C6 Glu)	0.800	0.794	0.834

reference spectra. The correlation coefficients were calculated using equation as follows:

$$r_{ab} = \frac{\sum |a_i \cdot b_i| - \frac{\sum a_i \sum b_i}{n}}{\sqrt{\left(\sum a_i^2 - \frac{(\sum a_i)^2}{n}\right) \left(\sum b_i^2 - \frac{(\sum b_i)^2}{n}\right)}}, \quad (15)$$

where r_{ab} is the correlation coefficient, a_i and b_i are the reference and the reconstructed spectra, respectively.

The correlation coefficient is a number between -1 and 1 which measures the similarity degree between two vectors. If the correlation coefficient is 0 , it means that there is no linear relationship between these two vectors. If it is 1 , the reference and estimate are identical and if it is -1 , the reference and estimate are mirror images.

The correlation coefficients between the reference and reconstructed pure component spectra obtained from the DECRA, PMF, and entropy minimization approaches for the first two spectral data sets are presented in Tables 1 and 2. However, the correlation coefficients for the third spectral data set are not shown since reference spectra were not available.

It is clear from these two tables above that the correlation coefficients for the gelatin compound derived obtained from these three techniques are all exactly the same. However, the correlation coefficients of TX-100 and di-(C6 Glu) obtained from the entropy minimization approach are higher than those obtained via DECRA and PMF. In addition, visual inspection of Figs. 3 and 5 shows the reconstruction qualities via entropy minimization for these two components slightly better than DECRA.

5. Conclusion

The general applicability of entropy-minimized curve resolution techniques has been re-confirmed, by successful extension from FTIR to NMR spectroscopy. Specif-

ically, the spectral estimates from NMR data are particularly good. Moreover, the resolution results from the current NMR data sets verify that the entropy minimization approach produces spectral estimates comparable to or better than the DECRA and PMF algorithms.

References

- [1] C.S. Johnson Jr., Diffusion ordered nuclear magnetic resonance spectroscopy: principles and applications, *Prog. Nucl. Magn. Reson. Spect.* 34 (1999) 203–256.
- [2] M.A. Delsuc, T.E. Malliavin, Maximum entropy processing of DOSY NMR spectra, *Anal. Chem.* 70 (1998) 2146–2148.
- [3] L.C.M. Van Gorkom, T.M. Hancewicz, Analysis of DOSY and GPC-NMR experiments on polymers by multivariate curve resolution, *J. Magn. Reson.* 130 (1998) 125–130.
- [4] M. Vives, R. Tauler, V. Moreno, R. Gargallo, Study of the interaction of a cis-dichloroaminopyrrolidine Pt(II) complex and the polynucleotide poly(I)–poly(C) acid by means of H-1-NMR and multivariate curve resolution, *Anal. Chim. Acta* 446 (2001) 439–450.
- [5] W. Windig, B. Antalek, Direct exponential curve resolution algorithm (DECRA): a novel application of the generalized rank annihilation method for a single spectral mixture data set with exponentially decaying contribution profiles, *Chemom. Intell. Lab. Syst.* 37 (1997) 241–254.
- [6] Y.L. Xie, P.K. Hopke, P. Paatero, Positive matrix factorization applied to a curve resolution problem, *J. Chemometrics* 12 (1998) 357–364.
- [7] H.L. Shen, C.Y. Airiau, R.G. Brereton, Resolution of on flow LC/NMR data by multivariate methods—a comparison, *J. Chemometrics* 16 (2002) 469–481.
- [8] W. Windig, B. Antalek, J.L. Lippert, Y. Batonneau, C. Bremard, Combined use of conventional and second-derivative data in the simplisma self-modeling mixture analysis approach, *Anal. Chem.* 74 (2002) 1371–1379.
- [9] L. Chen, Z. Weng, L.Y. Goh, M. Garland, An efficient algorithm for automatic phase correction of NMR spectra based on entropy minimization, *J. Mag. Res.* 158 (2002) 164–168.
- [10] C.E. Shannon, W. Weaver, *The Mathematical Theory of Communication*, The University of Illinois Press, Urbana, IL, 1949.
- [11] W. Weaver, Recent contributions to the mathematical theory of communication, in: C.E. Shannon, W. Weaver (Eds.), *The Mathematical Theory of Communication*, The University of Illinois Press, Urbana, IL, 1949, pp. 94–117.
- [12] K. Sasaki, S. Kawata, S. Minami, Constrained nonlinear method for estimating component spectra from multicomponent mixture, *Appl. Opt.* 22 (1983) 3599–3603.
- [13] K. Sasaki, S. Kawata, S. Minami, Estimation of component spectral curves from unknown mixture spectra, *Appl. Opt.* 23 (1984) 1955–1959.
- [14] S.D. Brown, A.M. Harper, Multivariate analysis of time-resolved pyrolysis mass spectral data, in: C.L. Wilkins (Ed.), *Computer Enhanced Analytical Spectroscopy*, vol. 4, 1993, pp. 135–163.
- [15] Y.Z. Zeng, M. Garland, An improved algorithm for estimating pure component spectra in exploratory chemometric studies based on entropy minimisation, *Anal. Chim. Acta* 359 (1998) 303–310.
- [16] Y. Pan, L. Susithra, M. Garland, Pure component reconstructions using entropy minimizations and variance-weighted piecewise-continuous spectral regions. Application to the unstable experimental system, *J. Chemometrics* 14 (2000) 63–77.

- [17] E. Widjaja, M. Garland, Pure component spectral reconstruction from mixture data using SVD, global entropy minimization and simulated annealing. Numerical investigations of admissible objective functions using a synthetic 7-species data set, *J. Comput. Chem.* 23 (2002) 911–919.
- [18] L. Chen, W. Chew, M. Garland, Spectral pattern recognition of in situ FT-IR spectroscopic reaction data using minimization of entropy and spectral similarity (MESS): application to the homogeneous rhodium catalyzed hydroformylation of isoprene, *Appl. Spectrosc.* 57 (2003) 491–498.
- [19] Internet-downloadable files at sun.mcs.clarkson.edu, in folder of `pub/hopkepk/data`.
- [20] G.H. Golub, C.F. Van Loan, *Matrix Computations*, Johns Hopkins University Press, Baltimore, 1996.
- [21] C.E. Shannon, A mathematical theory of communication, *Bell Syst. Tech. J.* 3 (1948) 379–423.
- [22] A. Corana, M. Marchesi, C. Martin, S. Ridella, Minimizing multimodal functions of continuous variables with the “Simulated Annealing” algorithm, *ACM Trans. Math. Softw.* 13 (1987) 262–280.