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NNLS AND MCR-ALS DECOMPOSITION OF RAMAN AND FTIR SPECTRA OF MULTICOMPONENT LIQUID SOLUTIONS

The possibilities of the decomposition by non-negative least squares (NNLS) and Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) methods of determination of spectra and concentrations of species in multicomponent (up to 8) liquid solutions by analyzing FTIR ATR and Raman spectra are discussed. It is shown that the NNLS decomposition of Raman spectra provides better results than the decomposition of the same mixture measured with the FTIR ATR method. This fact is connected with narrower width and smaller overlap of vibrational peaks obtained with the use of Raman spectroscopy comparing to IR spectroscopy for molecular liquids. It is shown that using the known spectra can increase the total number of species, for which a quantitative information can be successfully obtained. The unknown concentration profiles of an $N = 8$-component liquid mixture can be found correctly if the $N-1$ spectra of pure components are used as spectral constrains during the MCR-ALS analysis.

K e y w o r d s: Raman spectra, FTIR ATR spectra, multicomponent mixture, decomposition, multivariate curve resolution.

1. Introduction

Raman and IR spectroscopy can provide a quantitative information about the distribution of chemical compounds in an object under study [1]. The determination of a species concentration in multicomponent mixture from spectral data can be done by different chemometric techniques [1,2]. Most algorithms are based on the fact that the recorded spectra are the weighted sum of pure spectra of the components present in the investigated mixture. Based on this assumption, the unfolded data matrix $\mathbf{D}$ may be decomposed in a concentration matrix $\mathbf{C}$ and a spectra matrix $\mathbf{S}$

$$\mathbf{D} = \mathbf{C}\mathbf{S}^T + \mathbf{E}, \tag{1}$$

where $\mathbf{E}$ is the residual matrix.

When the pure spectrum of each component is known, the concentration of a component can be obtained, by directly using the classical least squares (CLS) approach [1]:

$$\mathbf{C} = \mathbf{D}\mathbf{S}\left(\mathbf{S}^T\mathbf{S}\right)^{-1}. \tag{2}$$

When at least one spectrum of species is unknown, the resolution techniques are applied [2]. Many proposed resolution algorithms were tested on real spectral data [3–6]. Among available algorithms, the multivariate curve resolution using the alternating least squares method (MCR-ALS) is most popular due to its simplicity in practical applications and a great flexibility in the incorporation of a prior information about the investigated system (e.g. non-negativity of spectral and concentration profiles, known spectra and concentration of species, closure conditions, *etc.*) [2, 7]. The comparison of different techniques using only a basic prior information about the system (non-negativity of profiles and closure condition) shows that the application of MCR-ALS is preferable [4, 5].

But the MCR-ALS solutions, as solutions of any other resolution technique, are not unique [8, 9]. There are two types of ambiguities realated to the intensity and the rotation. The presence of the intensity ambiguity implies that the estimated concentrations and spectra will be scaled by some unknown factors. This is not a serious problem in the qualitative analysis, but it may cause difficulties in the quantitative analysis, when the closure condition is
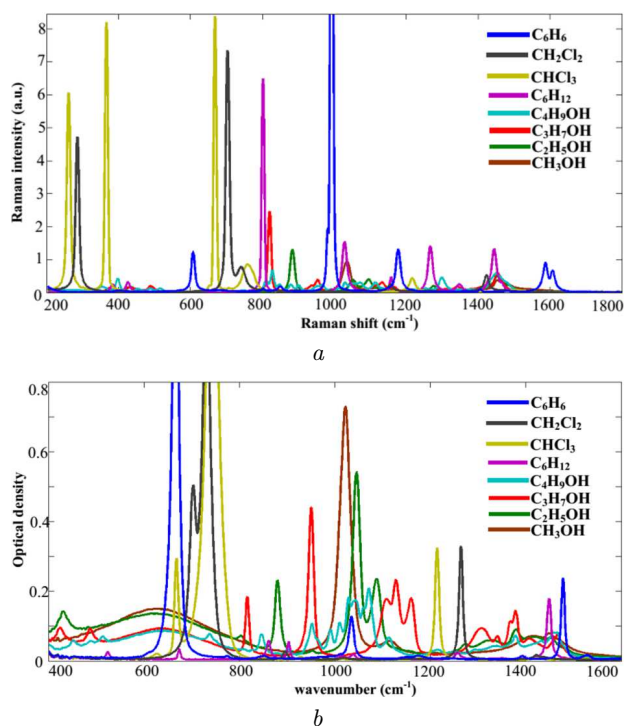
Fig. 1. Pure Raman (*a*) and ATR spectra (*b*) of 8 liquid components: methanol, ethanol, 2-propanol, 1-bythanol, cyclohexane, chloroform, dichloromethane, benzene

not applied. More critical is the rotation ambiguity which is always present, if there are two or more linearly independent overlapped components. It implies that the estimated spectrum for any of these components will be an unknown linear combination of the true components.

There were proposed methods of decreasing the rotational ambiguity based on a non-linear constrained optimization [10, 11]. These methods provide the band boundaries of feasible solutions. The complete resolution (without any ambiguities) is possible only in few cases: when local rank conditions [8] and selectivity [12] constraints are present.

In addition, the chemometric methods depend on solving a number of experimental and theoretical issues:

• ensuring the stability of a system during the measurement (time stability of the laser power, fluctuations of the detector sensitivity, mechanical vibration protection, *etc.*);

• resolution techniques work well only with small number of species (no more than 5–8 components);

• CLS may produce erroneous results, when spectral peaks are shifted and broadened due to the intermolecular interaction between components. It is sensitive also to the presence of noise. Thus, in some cases, the usage of the non-negative least squares (NNLS) method is preferred [13].

Recording the full spectra allows us to get a quantitative information about spectral and concentration profiles of components in an object under investigation. We have chosen a mixture of molecular liquids as a model system to study the decomposition of multicomponent mixtures.

2. Experiment

Sample preparation. Methanol, ethanol, 2-propanol, 1-bythanol, cyclohexane, chloroform, dichloromethane, and benzene with a purity of 99.9% were used in this research. Pure liquids were mixed at 11 different concentration ratios with accuracy better than 0.1 vol.%.

Raman spectroscopy. High levels of sensitivity and stability of the self-made Raman system have been achieved through the use of a stabilized diode laser StarBright 785 XM with a wavelength of 785 nm, a flat field spectrograph PI IsoPlane SCT-320, and a high sensitive stabilized CCD PI Pylon 400BR eXcelon cooled with liquid nitrogen.

All Raman spectra were measured with a spectral resolution of 3 cm^{-1} at an excitation wavelength of 785 nm. The laser power was 100 mW for every measurement.

FTIR spectroscopy. Reflection spectra in the mid-infrared region were registered, by using a FTIR spectrometer Nicolet iS50 equipped with a single-bounce diamond attenuated total reflection (ATR) accessory. All ATR spectra were measured with a spectral resolution of 4 cm^{-1}. The number of scans for each spectrum was 32. The obtained spectral resolution is quite enough to study the IR spectra of molecular liquids, where the half-width of vibrational bands is rarely smaller than 5 cm^{-1}.

3. Results

We used 8 different liquids for analysis: methanol, ethanol, 2-propanol, 1-bythanol, cyclohexane, chloroform, dichloromethane, and benzene. The measured Raman and IR spectra of pure liquids are shown in Fig. 1. The listed components were mixed with known
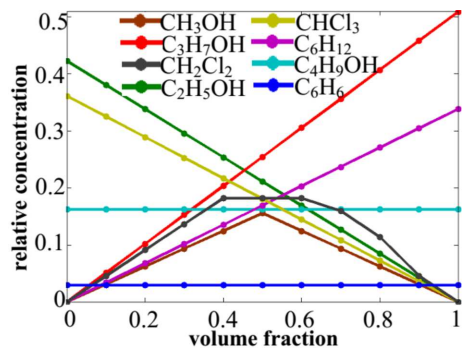
Fig. 2. Prepared concentration profiles for 11 liquid mixture samples each consisting of 8 components

a

b

Fig. 3. Concentration profiles obtained from Raman (*a*) and ATR (*b*) spectra as a result of the algorithmic decomposition of 11 mixture samples consisting of 8 liquid components
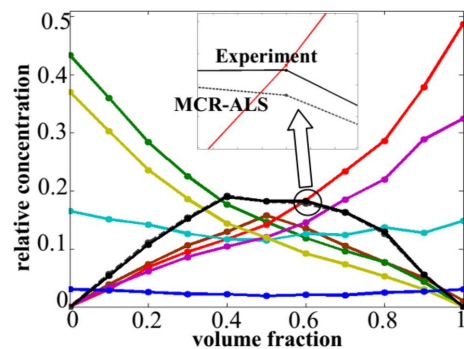

Fig. 4. Concentration profiles resulting from the MCR-ALS analysis of 11 mixture samples consisting of 8 liquid components with 7 known spectral profiles (dichloromethane assumed to be unknown)
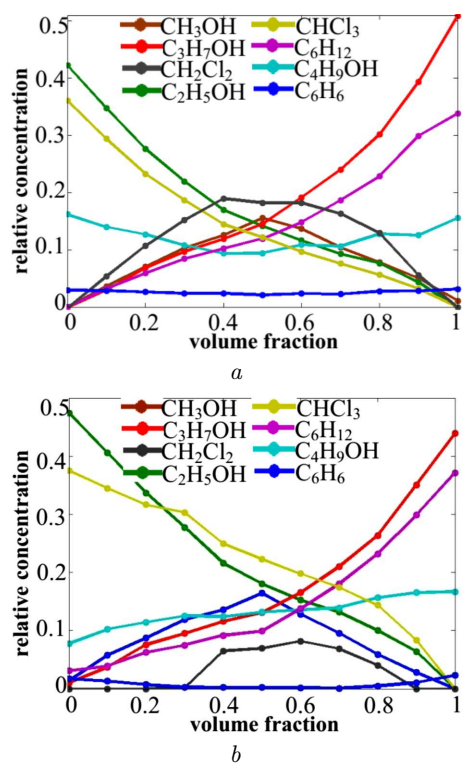

Fig. 5. Spectral profiles of dichloromethane as a result of the MCR-ALS analysis with the known spectral profiles of 7 other components

concentrations. The concentration profiles of 11 prepared samples each having 8 components are shown in Fig. 2. The concentration profiles as a result of the NNLS decomposition of 11 samples are shown in Fig. 3. Comparing Fig. 2 and Fig. 3, it is possible to conclude that Raman spectroscopy (Fig. 3, *a*) provides better data for the decomposition than IR spec-
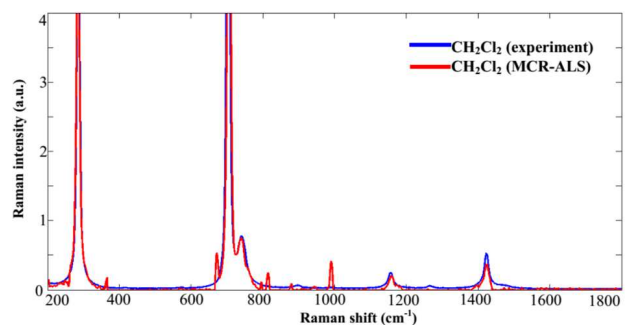
troscopy (Fig. 3, *b*). This fact is related to a narrower width and a smaller overlap of vibrational peaks in Raman spectra for molecular liquids. The resulting decomposition error (nonlinearity of the profiles of curves in Fig. 3, *a*) can be explained by the effects of peak shifting and broadening due to the intermolecular interaction between components. Such inherently nonlinear behavior cannot be accounted for by the simple NNLS decomposition.

It is known that the MCR-ALS method works well with a small number of species [3–5]. Our tests show that the curve resolution of an eight component mixture is a too difficult task for performing the full MCR analysis, if all spectra and concentrations profiles are unknown. But when the object under investigation has components with known vibrational spectra, they can be used in MCR-ALS as constrains (fixed values) in the rows of the matrix of spectra **S**. In accordance with this approach, the analysis of the 8-component

mixture with 7 fixed spectra of pure components was preformed. The dichloromethane spectrum was assumed to be unknown. In order to further improve the MCR results, we used the concentration profiles of 7 known components (except dichloromethane) as initial data for MCR-ALS iterations. The resulting concentration and spectral profiles are shown in Figs. 4 and 5. It is clearly seen that the profiles are very close to real values. MCR computations were performed in MATLAB GUI developed by Tauler's group [14].

4. Conclusions

The usage of known spectra was tested for multicomponent liquid mixtures. This procedure can increase the total number of species, for which a quantitative information can be successfully obtained: unknown concentration profiles of an $N = 8$-component liquid mixture can be found correctly if $N - 1$ spectra of pure components are used as spectral constrains in the MCR-ALS analysis.

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NNLS І MCR-ALS ДЕКОМПОЗИЦІЯ
СПЕКТРІВ КОМБІНАЦІЙНОГО РОЗСІЯННЯ
ТА ІНФРАЧЕРВОНОГО ПОГЛИНАННЯ
БАГАТОКОМПОНЕНТНИХ РІДКИХ РОЗЧИНІВ

Р е з ю м е

В роботі обговорюються можливості декомпозиції ІЧ спектрів порушеного повного внутрішнього відбиття (ППВВ) та спектрів КРС багатокомпонентних (до 8-ми складових) розчинів рідин з використанням таких методів, як найменші квадрати з обмеженням на не негативність спектрів і багатовимірне розділення кривих з використанням найменших квадратів, що чергуються. Показано, що декомпозиція за методом найменших квадратів з обмеженням на не негативність спектрів дає кращі результати у випадку аналізу спектрів КРС в порівнянні з ІЧ спектрами. Даний факт пов'язаний з тим, що спектри КРС рідин мають меншу півширину коливальних смуг, ніж ІЧ спектри і, відповідно, менше перекриття піків. Було показано, що використання спектрів відомих складових досліджуваного розчину в процесі декомпозиції дозволяє збільшити загальне число компонент розчину без втрати якості кількісного аналізу. Коректне знаходження концентраційних профілів в N-компонентному розчині ($N = 8$) може бути здійснено у випадку використання $N - 1$ спектральних профілів у ролі обмежень на спектри під час аналізу методом багатовимірного розділення кривих з використанням найменших квадратів, що чергуються.