Chemometric analysis of mixtures in molecular aggregated systems

Takafumi SHIMOAKA

Division of Environmental Chemistry, Institute for Chemical Research, Kyoto University
Gokasho, Uji, Kyoto 611-0011, Japan

E-mail: shimoaka@scl.kyoto-u.ac.jp

Separation, identification and quantification of chemical substances in a mixture are fundamental and important concepts in analytical chemistry. In order to understand properties of molecular aggregated systems, for example, the constituents and their quantity need to be investigated. Chemometric analyses of spectroscopic data have a great advantage of providing the quantity information from a set of spectra without actually separating the mixture into the individual constituents [1]. In particular, multivariate curve resolution (MCR) technique gives not only quantity of the constituents but also the corresponding spectra, which enable identification and also give information about chemical structure, molecular aggregates and molecular interaction.

Shimada et al. determined the chemical structures of a widely used pH indicator of bromothymol blue (BTB), which have long been under controversy, by employing a combined technique of chemometric analysis of UV–Vis spectra and quantum chemical calculations [2]. They also revealed the chemical structures of thymol blue (TB) by the same combined technique [3]. Although their experiments were quite simple, i.e., UV–Vis spectral measurements of aqueous solutions of the pH indicators, it is unique in that both the chemical structures and quantity changes were elucidated by using chemometrics.

Okajima et al. revealed that pure water has three distinct forms with different hydrogen bonding states and temperature-dependent quantity changes of the three forms by chemometric analysis of Raman spectra in the temperature range of -23 ~ 45°C [4]. Of interest that the density maximum at 4°C, which is one of the anomalies of water, is well explained by one of the forms, nanometer-sized ice crystals. Watanabe et al. applied chemometrics to Raman spectra of a mixture of *N*-methylimidazole (C1Im) and acetic acid in various molar ratios, and the spectral variation was revealed to be explained by three chemical species, ion pair, hydrogen bonded molecular complex and neat C1Im, which explains concentration-dependent changes in ionic conductivity [5]. These results indicate that the combination of chemometrics and vibrational spectroscopy is appropriate for investigating molecular aggregates and molecular interaction.

Thin film samples on a solid substrate have long been recognized not to be suitable for chemometric analysis, because the molecular orientation also influences the peak intensity via

the surface selection rules. Shioya et al. established a method to quantitatively investigate chemical reactions in thin films by using infrared MAIRS spectrometry [6].

Thus, chemometrics is a powerful tool in obtaining chemically important information, which can be applied to a variety of molecular aggregated systems, regardless of spectroscopic methods [7,8]. Another advantage is that chemometrics can remove noise and optical fringes from spectra that would otherwise interfere with analysis [9–11]. In recent years, many practical tools for chemometrics are available for general-purpose programming languages [12]. It is expected that chemometrics will be more widely used by analytical scientists, which should contribute to reveal various scientific phenomena.

References

1. Y. Morisawa, Anal Sci **35**, 833 (2019)

2. T. Shimada, T. Hasegawa, Spectrochim. Acta A: Molecular and Biomolecular Spectroscopy **185**, 104 (2017)

3. T. Shimada, K. Tochinai, T. Hasegawa, Bull. Chem. Soc. Jpn. **92**, 1759 (2019)

4. H. Okajima, M. Ando, H. Hamaguchi, Bull. Chem. Soc. Jpn. **91**, 991 (2018)

5. H. Watanabe, N. Arai, H. Jihae, Y. Kawana, Y. Umebayashi, J. Mol. Liq. **352**, 118705 (2022)

6. N. Shioya, R. Fujiwara, K. Tomita, T. Shimoaka, T. Hasegawa, J. Phys. Chem. A **124**, 2714 (2020)

7. Y. Ozaki, Anal. Sci. **37**, 1193 (2021)

8. M. Saeki, T. Yomogida, D. Matsumura, T. Saito, R. Nakanishi, T. Tsuji, H. Ohba, Anal. Sci. **36**, 1371 (2020)

9. Y. Kusaka, T. Hasegawa, H. Kaji, J. Phys. Chem. A **123**, 10333 (2019)

10. N. Shioya, T. Shimoaka, T. Hasegawa, Anal. Sci. **33**, 117 (2017)

11. T. Shimoaka, T. Hasegawa, J. Mol. Liq. **223**, 621 (2016)

12. S. Morita, Anal Sci **36**, 107 (2020)