Application Note

No. 080AT0180-E

Two-Dimensional Infrared Correlation Analysis of Maillard Reaction (Non-Enzymatic Browning)

Introduction

Two-dimensional correlation analysis is employed as a method for representing 3D spectra such as time-variance spectra in an easy-to-see manner. In the case of IR 3D spectra, it is possible to analyze the correlation between functional groups by drawing the spectrum on both the x and y-axes and then viewing the band correlation that can be observed for each spectrum. As an example, structural changes in samples as a result of changes in time and temperature are measured as 3D spectra. The obtained time resolved spectra are Fourier-transformed in the time direction, and then the correlation strength is computed and plotted using the real part and imaginary part. The correlation strength of the real part and the imaginary part is known as synchronous correlation and asynchronous correlation, respectively. Analyzing both correlation spectra makes it possible to estimate structural change in substances. And by combining infrared analysis with other forms of spectral analysis, including near-infrared spectroscopy and Raman spectroscopy, it is possible to study peak assignment and the relationship between intramolecular and lattice vibrational modes. This time we employed two-dimensional spectroscopy to analyze the Maillard reaction, which is well known as a non-enzymatic browning reaction in food (see the Application Note (080AT0179)).

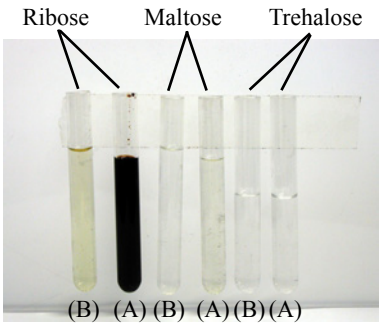
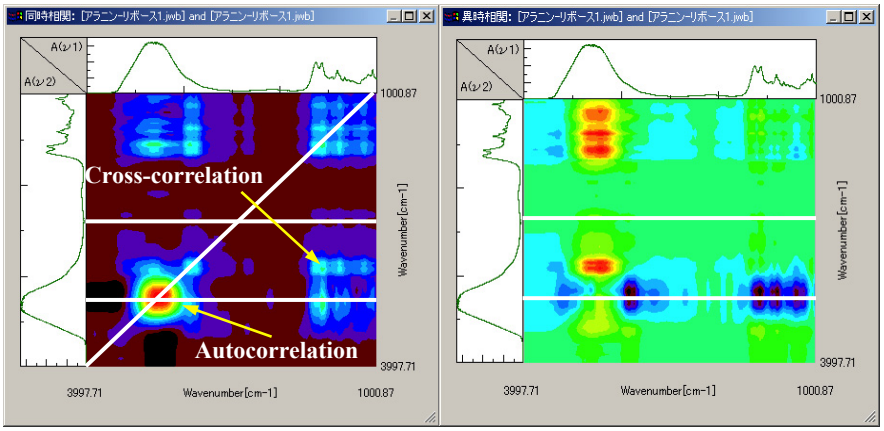
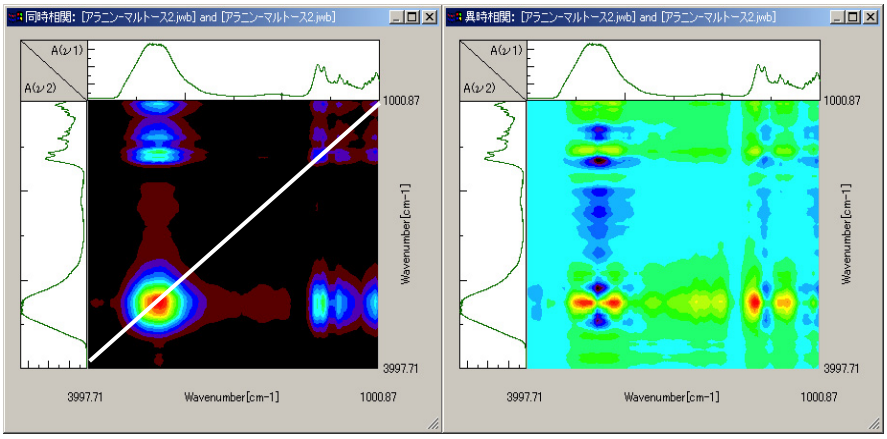


Figure 1 Photo of sample solution before (B) and after (A) reactions



Synchronous correlation Asynchronous correlation

Figure 2 Synchronous and Asynchronous Correlation of Ribose



Synchronous correlation Asynchronous correlation

Figure 3 Synchronous and Asynchronous Correlation of Maltose

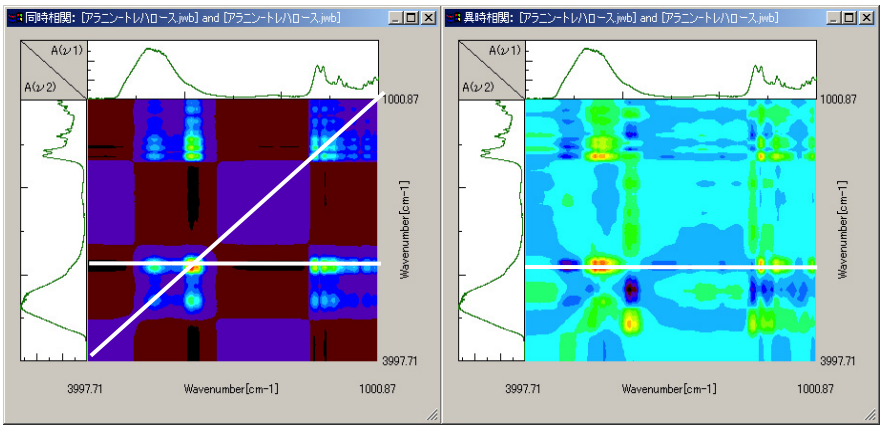
JASCO INTERNATIONAL CO., LTD.
4-21, Sennin-cho 2-chome, Hachioji, Tokyo 193-0835, Japan
Tel: +81-42-666-1322, Fax: +81-42-665-6512

Experimental

Ribose, maltose, and trehalose aqueous solutions (3 mol/L) were each mixed with a ß-alanine aqueous solution (3 mol/L), and then each mixture was heated at 80ºC for 30 minutes while measuring the IR time-variance spectra (For more information, see the Application Note 080AT0179. Two-dimensional spectroscopy was then used to analyze the results.

Results and Discussions

Figure 1 is a photo showing thepre- and post-reaction sample solutions. Based on this photo, it was verified that the nonreducing sugar trehalose alone was not experiencing the Maillard reaction. Figures 2 to 4 illustrate the synchronous and asynchronous correlation spectra for each type of sugar (warm colors are positive). Synchronous correlation is generally used to evaluate whether peak strength variation is exhibiting the same changes due to perturbation. It is thought that in synchronous correlation, the higher the strength of the autocorrelation peaks (two with same wavenumbers), the greater the change due to perturbation. In addition, cross-correlation peaks (two with the different wavenumbers) take on a positive value when they rise or fall in the same direction due to perturbation and a negative value when they move in opposite directions. Asynchronous correlation has a complementary relationship with synchronous correlation, and it only has cross-correlation peaks. A cross-correlation peak in this case means one that varies at different times, or more precisely, one that takes on a negative value (or positive in the opposite case) when peak strength change on the x axis occurs at an earlier time than on the y axis. In the synchronous correlation for ribose and maltose, a strong autocorrelation near 3500 cm^{-1} was seen, which is thought to be an OH or NH base, but this was not verified for trehalose. This tells us that OH or NH bases are related to the Maillard reaction. It also indicates that in the synchronous correlation of ribose and maltose, the peaks of the respective sugars rise or fall in the same direction based on the fact that they have positive correlations at 3500 cm^{-1} and 1560 cm^{-1}. It is also thought that based on the asynchronous correlation of ribose, the changes at 2800 and 1540 cm^{-1} occur before the OH and NH base changes (which are likely at 3300 cm^{-1}) because the vicinity of 2800 and 1540 cm^{-1} on the x axis shows a negative correlation to 3300cm^{-1} on the y axis. In the asynchronous correlation of maltose, the opposite of what occurs with ribose happens. Based on the synchronous correlation of trehalose, we can verify that the CH base peak at 2900 cm^{-1} greatly varies over time. We can also verify that in the asynchronous correlation of trehalose, the CH base peak at 2900 cm^{-1} varies over time after the OH base and water peak changes occur based on the fact that the peaks at 3300 and 1640 cm^{-1} on the x axis show a positive value versus the peak at 2900 cm^{-1} on the y axis. Using two-dimensional spectroscopy in this manner makes it possible to, among other things, analyze reactions in details.



Synchronous correlation Asynchronous correlation

Figure 4 Synchronous and Asynchronous Correlation of Trehalose

Reference: Noda, Isao and Ozaki Yukihiro, “Spectral Research”, 1995: 44