Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Frequency division multiplex HPLC-MS for simultaneous analyses

Hiroka Kishi, Takashi Kumasaki, Shinya Kitagawa*, Hajime Ohtani

Department of Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan

Content:

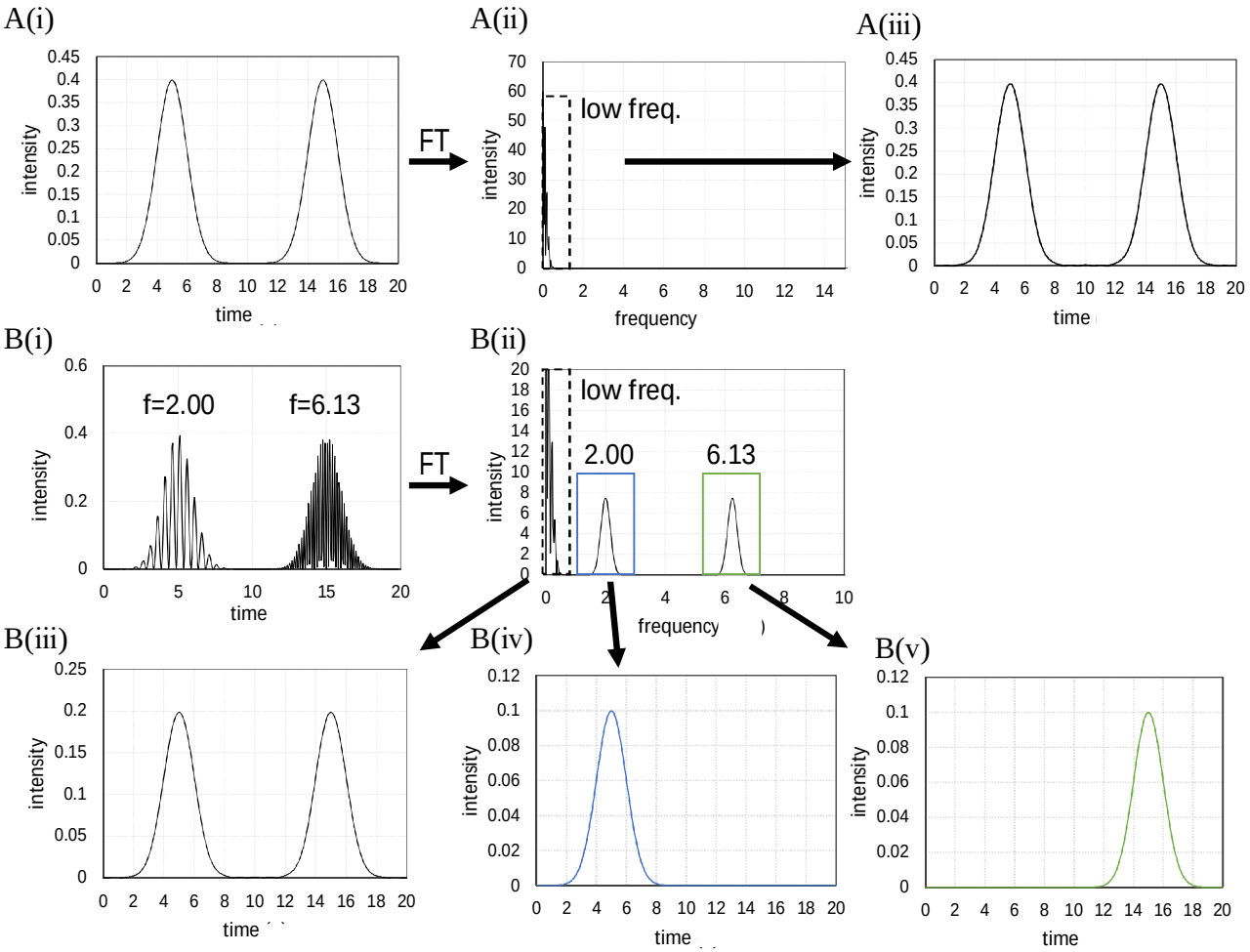

Figure S1. (A) Virtual chromatogram without modulation (i), its power spectrum obtained by FT (ii), and the restored-chromatogram for low frequency region. (B) Virtual chromatogram with different frequency modulations (2.00 and 6.13 Hz) (i), its power spectrum obtained by FT (ii), and its restored-chromatogram by RFT for low frequency (iii), 2.00 Hz (iv), and 6.13 Hz (v) regions. The figures with the exception of (A-iii) and (B-iii) are shown in Figure 1.

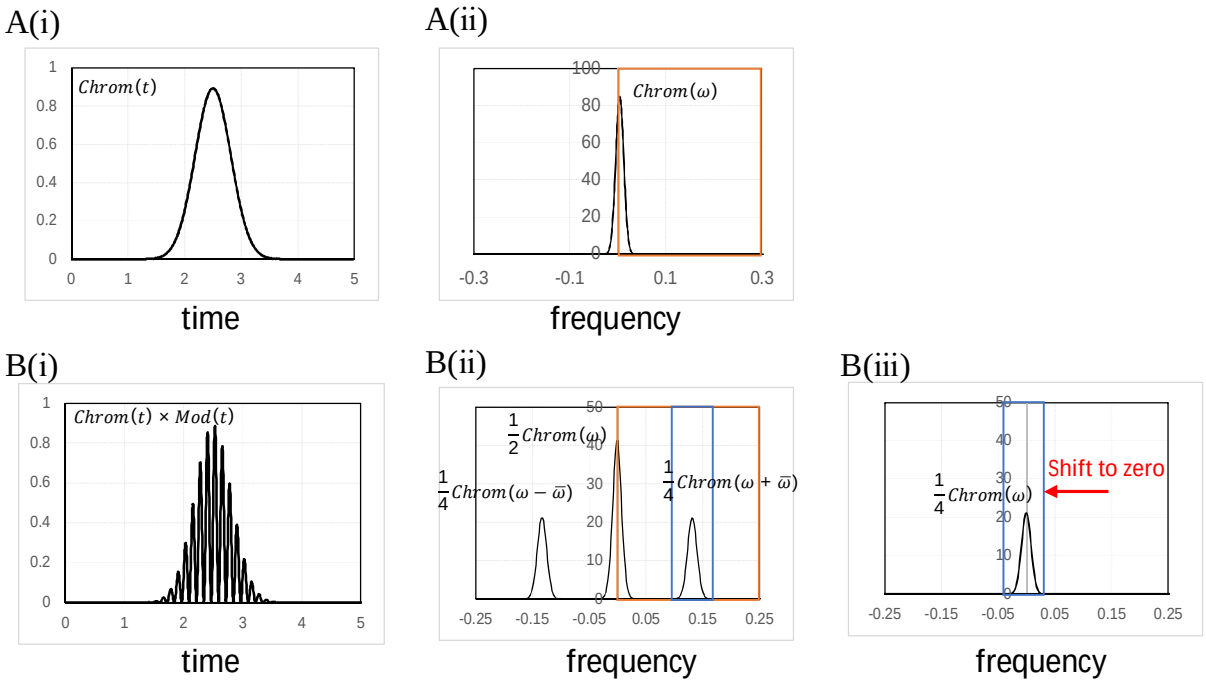

Figure S2. (A) Chromatogram without modulation (i) and its power spectrum with both plus and minus frequency regions (ii). In the text, only the pulse frequency region (in the orange box) is presented. (B) Chromatogram with modulation (i) and its power spectrum with both plus and minus frequency regions (ii). The blue box in (B-ii) denotes the signal for extraction. Before RFT, the signal is shifted to $f = 0$ region (B-iii). The following equations describe a mathematical detail of the signal processing with a typical modulation function of Mod(t).

$$Chrom(t) = \frac{1}{2}a_0 + \sum(a_i \cos(\omega_i t) + b_i \sin(\omega_i t)) \overset{FT}{\Rightarrow} Chrom(\omega) \overset{RFT}{\Longrightarrow} Chrom(t)$$

$$Mod(t) = \frac{1}{2}(1 + \cos(\bar{\omega}t))$$

$$Chrom(t) \times Mod(t) = \frac{1}{2}Chrom(t) + \left\{\frac{1}{4}a_0 \cos(\bar{\omega}t) + \frac{1}{2}\sum(a_i \cos(\omega_i t) + b_i \sin\omega_i t)\cos(\bar{\omega}t)\right\}$$

$$= \frac{1}{2}Chrom(t) + \left\{\frac{1}{4}a_0 \cos(\bar{\omega}t) + \frac{1}{2}\sum(a_i \cos(\omega_i t)\cos(\bar{\omega}t) + b_i \sin(\omega_i t)\cos(\bar{\omega}t))\right\}$$

$$= \frac{1}{2}Chrom(t) + \left\{\frac{1}{4}a_0\left(\frac{1}{2}\cos(\bar{\omega}t) + \frac{1}{2}\cos(-\bar{\omega}t)\right) + \frac{1}{2}\sum\left(a_i\frac{\cos(\omega_i t + \bar{\omega}t) + \cos(\omega_i t - \bar{\omega}t)}{2} + b_i\frac{\sin(\omega_i t + \bar{\omega}t) + \sin(\omega_i t - \bar{\omega}t)}{2}\right)\right\}$$

$$= \frac{1}{2}Chrom(t) + \frac{1}{4}\left\{\frac{1}{2}a_0\cos(\bar{\omega}t) + \sum(a_i \cos(\omega_i t + \bar{\omega}t) + b_i \sin(\omega_i t + \bar{\omega}t)) + \frac{1}{2}a_0\cos(-\bar{\omega}t) + \sum(a_i \cos(\omega_i t - \bar{\omega}t) + b_i \sin(\omega_i t - \bar{\omega}t))\right\}$$

$$\overset{FT}{\Rightarrow}\frac{1}{2}Chrom(\omega) + \frac{1}{4}Chrom(\omega + \bar{\omega}) + \frac{1}{4}Chrom(\omega - \bar{\omega})$$

$$\overset{extraction}{\Longrightarrow}\frac{1}{4}Chrom(\omega + \bar{\omega}) \overset{zero\ shift}{\Longrightarrow}\frac{1}{4}Chrom(\omega) \overset{RFT}{\Longrightarrow}\frac{1}{4}Chrom(t)$$

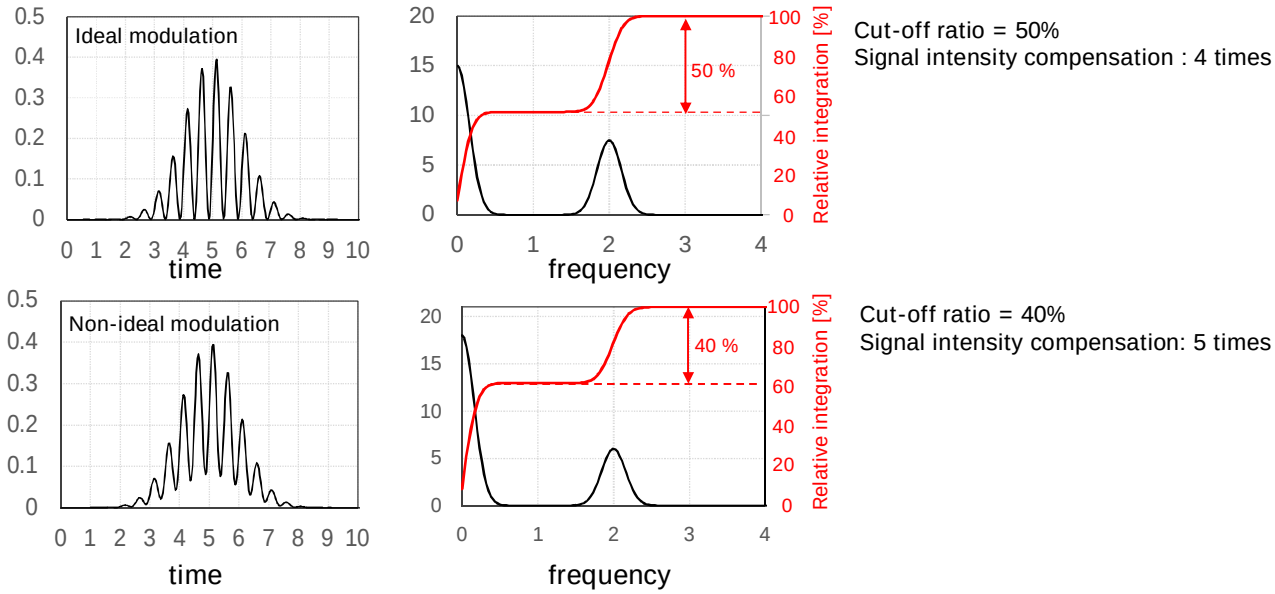

Figure S3. Evaluation of a cut-off ratio using integration curve of the power spectrum to compensate the signal intensity of a restored chromatogram.

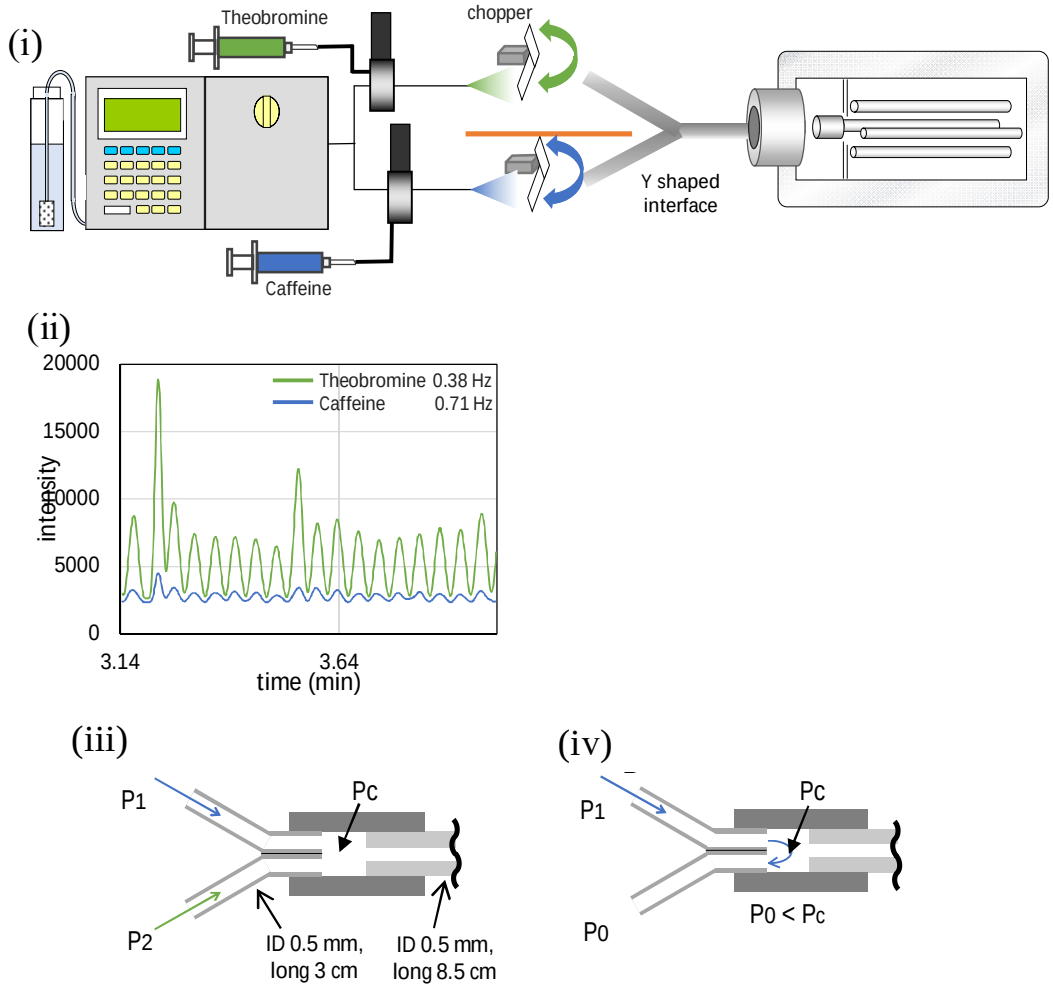

Figure S4. Mechanism of interference used in two chopper type modulators. (i) apparatus used for the experiment (continuous injection mode without separation column), (ii) signals are recorded in the same phase, (iii) both gas stream are not blocked by the choppers and both analytes were detected, (iv) lower (green) gas stream (and analyte stream) was blocked by the chopper. Since P_0 is less than P_c, the buck flush of the analytes (denoted with blue) suppressed the signal intensity of the blue analytes observed in MS.

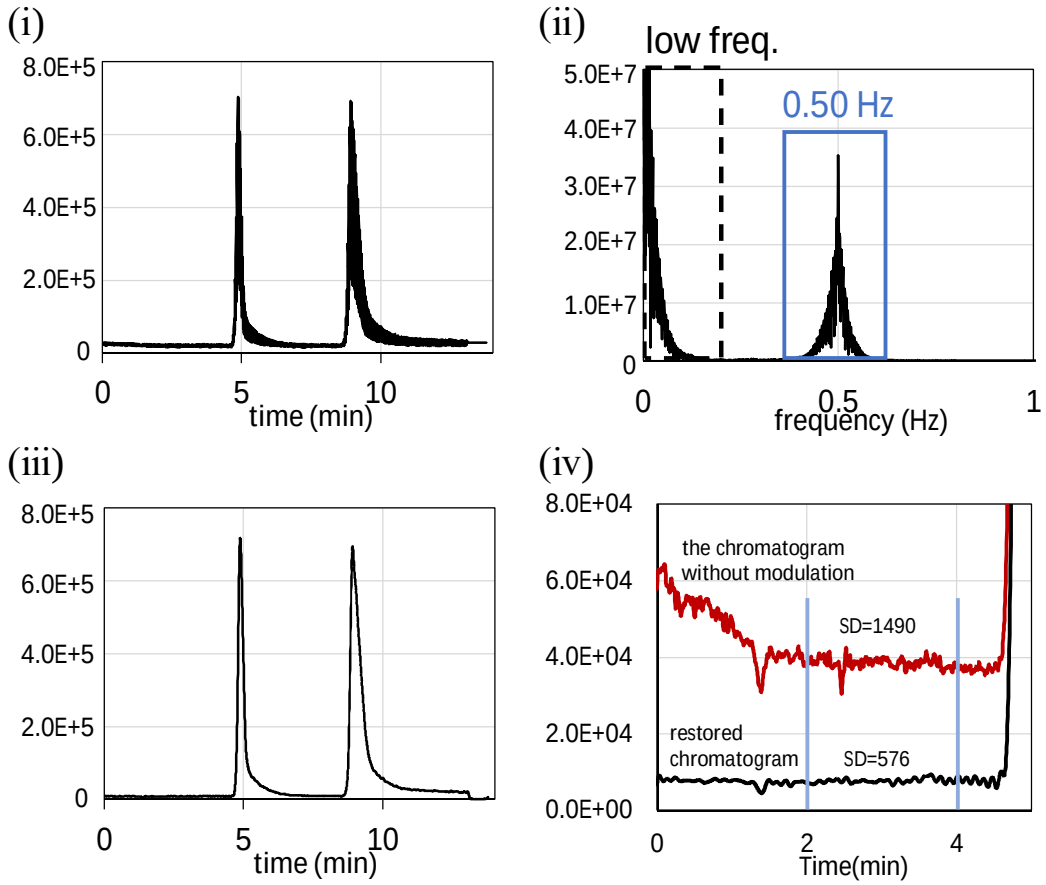

Figure S5. Chromatogram obtained by 1HPLC-1MS with modulation via an ion-gate type modulator (0.5 Hz) (i), its power spectrum obtained by FT (ii), and the restored-chromatogram by RFT for the 0.5 Hz region (iii).

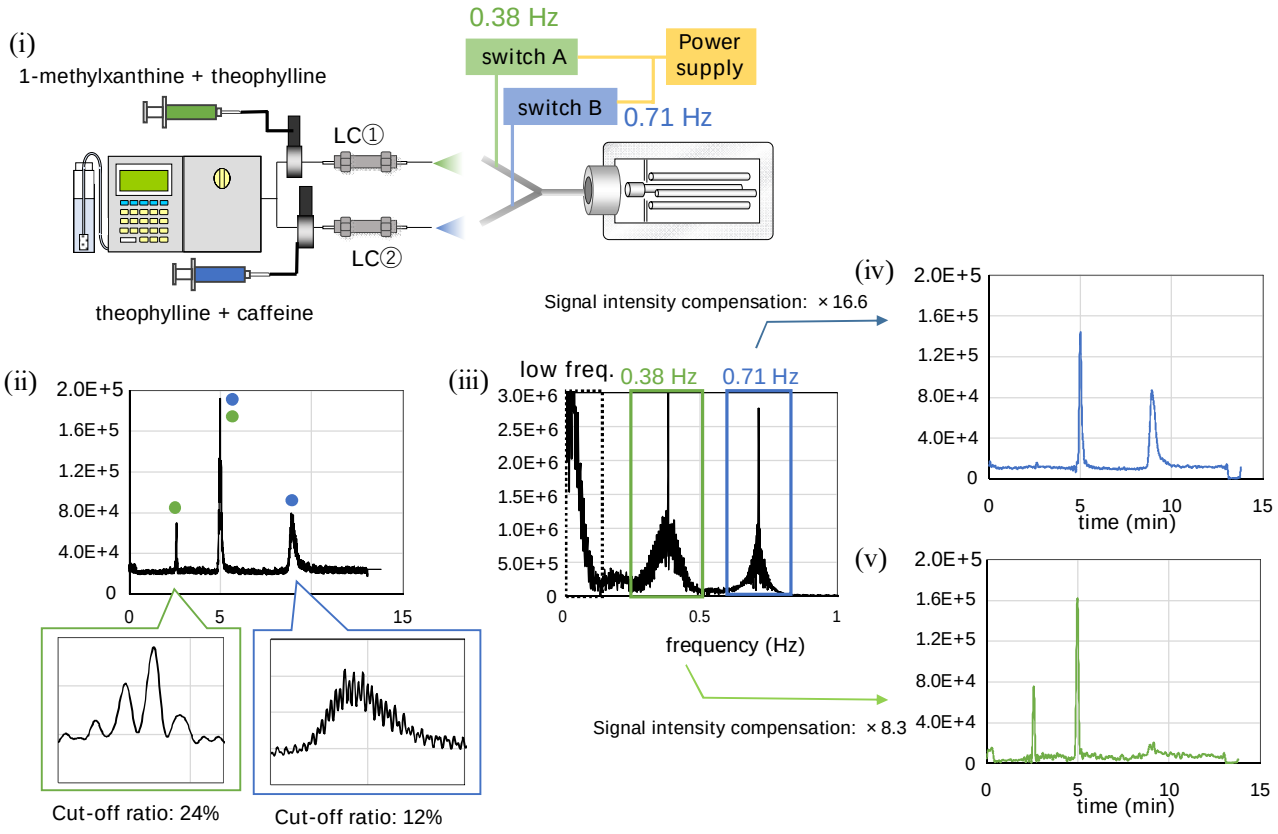

Figure S6. Simultaneous analysis of mixtures of (1) 1-methylxanthine and theophylline, and (2) theophylline and caffeine in 2LC-1MS. (i) schematic diagram of the experiment, (ii) a mixed-chromatogram, (iii) a power spectrum of (ii), (iv) a restored-chromatogram for 0.71 Hz region with signal intensity compensation of 16.6 times, and restored-chromatogram for 0.38 Hz with signal intensity compensation of 8.3 times.