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Intelligent Peak and Spectrum Deconvolution Using Photodiode Array Detector

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P-126

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1. INTRODUCTION

A novel data analysis technique named i-PDeA Ⅱ (Intelligent Peak Deconvolution Analysis Ⅱ) has been developed for extracting two or more target peaks from unseparated peaks using data from three-dimensional photodiode array (PDA) detector with a multivariate curve resolution-alternating least squares (MCR-ALS). It also employs an expectation maximization (EM) algorithm with a bidirectional exponentially modified Gaussian (bemg) model function as a constraint for chromatograms and a huge number of PDA spectra aligned with the time axis. The i-PDeA Ⅱ function can automatically extract respective peak profiles and absorption spectra from unseparated elution band. Through this investigation, we confirm the following issues that reveal accuracy, precision, and applicability of i-PDeA Ⅱ.

1) Deconvolution for 2-component system

2) Deconvolution for 3-component system with greatly different abundance ratio

3) Investigation of the relationship between resolution and deconvolution accuracy

4) Practical applications of i-PDeA Ⅱ

2. MATHEMATICAL BACK GROUND

3D data composition

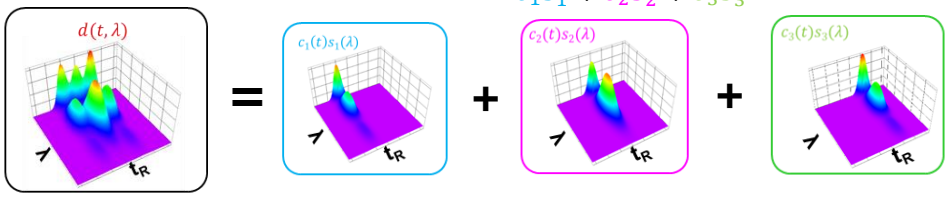
Ideal 3-compont system is expressed by vector product of 3 peak profiles and 3 spectra → Matrix expression

$$\boldsymbol{d}_i^T = \alpha_i \boldsymbol{s}_1^T + \beta_i \boldsymbol{s}_2^T + \gamma_i \boldsymbol{s}_3^T = (\alpha_i \quad \beta_i \quad \gamma_i) \begin{pmatrix} \boldsymbol{s}_1^T \\ \boldsymbol{s}_2^T \\ \boldsymbol{s}_3^T \end{pmatrix}$$

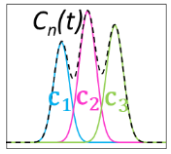
3 components system

$$D = \boldsymbol{c}_1 \boldsymbol{s}_1^T + \boldsymbol{c}_2 \boldsymbol{s}_2^T + \boldsymbol{c}_3 \boldsymbol{s}_3^T$$

Measured 3D data



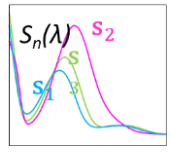
Peak profile



Retention time

×

Spectrum



Wavelength

$$D = \boldsymbol{c}_1 \boldsymbol{s}_1^T + \boldsymbol{c}_2 \boldsymbol{s}_2^T + \cdots + \boldsymbol{c}_N \boldsymbol{s}_N^T$$

N-components system

$$D = CS^T$$

Matrix expression

C: real peak profiles, S^T: real spectra

3D data expression by estimation

Estimation accompanies error *E*

$$D = C_E S_E^T + E$$

C_E: estimated peak profiles, S_E^T: estimated spectra, E: Error

$$E^2 = \left(D - \Sigma f_k S_k^T\right)^2$$

Minimizing square error E^2 by MCR-ALS and EM Component number is automatically optimized

$\boldsymbol{s}_k^T$ =Each spectrum ← Real spectra at the beginning and/or the ending of the elution band

$f_k = bemg(t,a,b)$ ← Mathematical model for peak profile (Considering both peak tailing and leading)

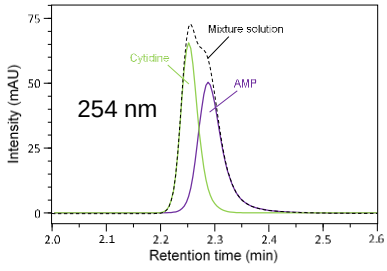
$$emg(t,b) = \int_0^\infty e^{-bx} * e^{-(t-x)^2} dx$$

$$f(k) = bemg(t,a,b) = \int_{-\infty}^0 e^{ax} * emg(t-x,b) dx$$

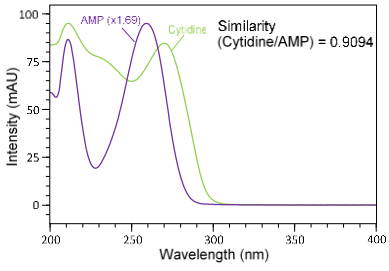
3. EXPERIMENTS AND RESULTS(1)

2-component system
Deconvolution of Cytidine and AMP

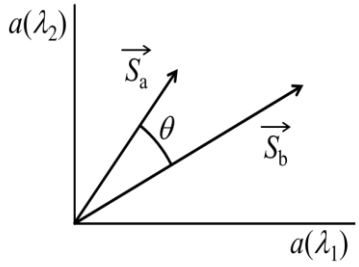
Chromatograms



Spectra

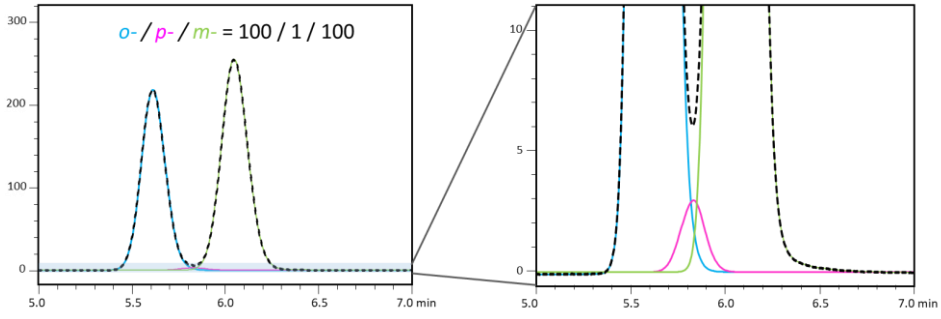


Similarilty = $cos\theta$ = $\dfrac{S_1 \cdot S_2}{|S_1||S_2|}$



Component	Individual		Mixture (Deconvolution)		Error %	Similarity
	Area(μAU•s)	%RSD (n=6)	Area(μAU•s)	%RSD (n=6)		
Cytidine	154,514	0.14%	154,934	2.46%	0.27%	1.0000
AMP	171,643	0.22%	168,590	2.79%	-1.78%	0.9995

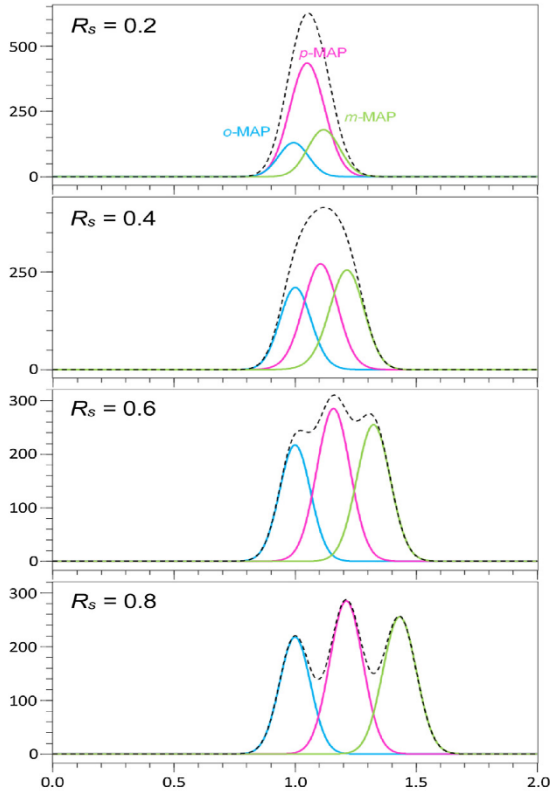
3-component system in different abundance ration
Deconvolution of *o*-, *m*-, *p*-(MAP)
(Abundance ration; 100/100/1)



Component	Area (μAU•s)		Error %	Similarity
	Individual	Mixture		
o-MAP	2,090,806	2,080,405	-0.50%	1.0000
p-MAP	27,666	26,639	-3.71%	0.9996
m-MAP	2,658,837	2,656,836	-0.08%	1.0000

3. EXPERIMENTS AND RESULTS(2)

Relationship between peak resolution and deconvolution accuracy
Deconvolution for *o*-, *m*-, *p*-MAP



(*o*- / *m*- / *p*- : equivalent abundance ratio)

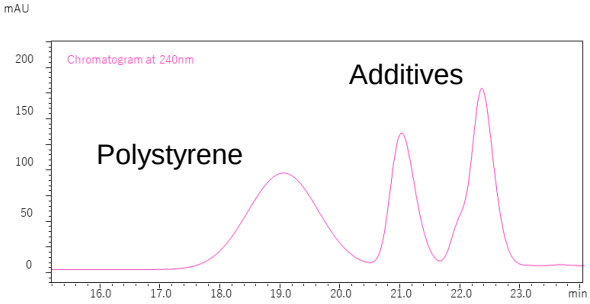
Resolution		***o-MAP***	***m-MAP***	***p-MAP***
	Individual	2.091	2.937	2.658
0.2	Area	1.204	4.698	1.784
	Error	-42.41 %	+59.98 %	-32.90 %
0.4	Area	2.046	2.900	2.740
	Error	-2.16 %	-1.23%	+3.06%
0.6	Area	2.083	2.950	2.652
	Error	-0.36 %	+0.46 %	-0.23 %
0.8	Area	2.091	2.936	2.658
	Error	0.00 %	0.00 %	0.00 %

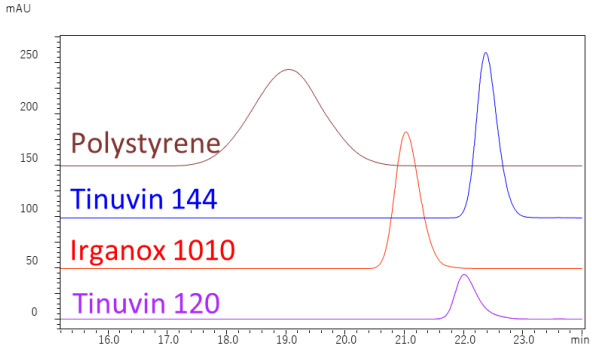
※ Area: x 10^6 (μV・sec)

Intelligent Peak and Spectrum Deconvolution Using Photodiode Array Detector

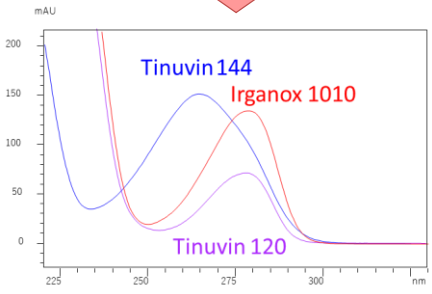
3. EXPERIMENTS AND RESULTS(3)

Polymer additives in SEC





Deconvolution of three additives (PDA)

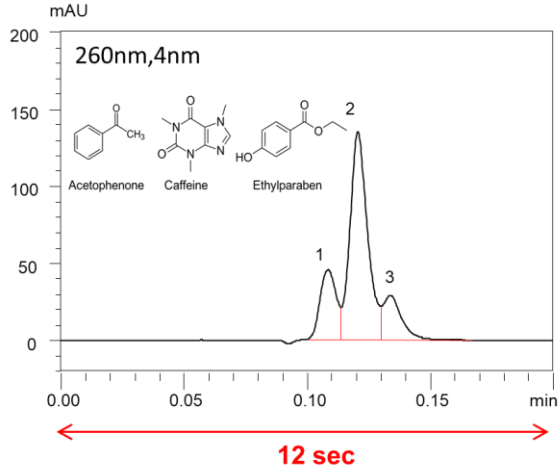


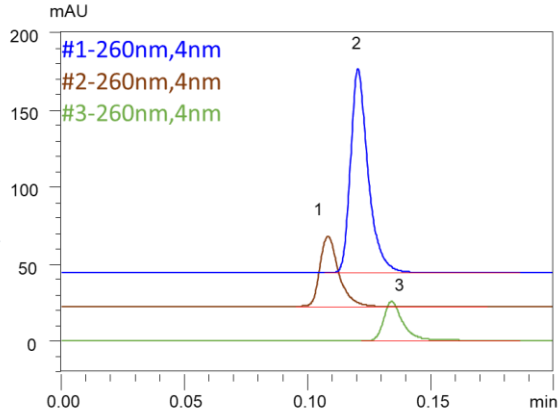
Deconvoluted Spectra

Additive	Irganox 1010	Tinuvin 144	Tinuvin 120
Linearity of calibration curve (r^2)	0.999	0.995	0.998
Determined content (mg/g)	49.2	23.1	27.4
%RSD	1.28	1.93	1.47

From 0.01 to 0.1% (w/v), n=6

Ultra high speed separation





Component	t_R	*Individual*	*Deconvolution*		*Vertical cut*	
		Area	*Area*	*Error*	*Area*	*Error*
1.Caffeine	0.109	24680	24812	+0.5%	20486	-12.8%
2.Ethylparaben	0.121	65368	66111	+1.1%	66812	+2.9%
3.Acetophenone	0.134	13679	13912	+1.7%	15010	+13.1%

4. CONCLUSIONS

1. i-PDeA II, an algorithm for reliable chromatographic peak deconvolution was developed by applying the MCR-ALS to PDA data.
2. Ultra fast and accurate quantitative analysis is possible at any desired wavelength even with incomplete separation.
3. i-PDeA II can be applied to analysis of isomers with identical molecular weights. It would be an alternative of MS detection for components that have identical *m/z* values.
4. Reliable spectral data analysis can be done even after peak deconvolution.

Reference

S. Arase et.al, *J. Chromatgr A 1469(2016) 35*

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