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Investigation of 2D Correlation Fluorescence Spectrum of Pesticide Residual in Tea

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ABSTRACT

In this paper, the characteristics of 2D correlation fluorescence spectrum of three pesticides (dicofol, carbofuran and fenvalerate) residue in tea are investigated. With different perturbation of excitation wavelength and concentration respectively, the cross-peaks and auto-correlation-peaks of 2D correlation fluorescence spectrum of dicofol are studied. Besides, with the same perturbation of concentration, the features of 2D correlation spectrum of carbofuran and fencalerate are researched. In addition, a series of statistical features of 2D correlation spectral image are discussed which indicating the distribution characteristics. In a word, all the characteristics of signal peaks and statistical features serve as a basis for identification of pesticide.

1. Introduction

Dicofol is an efficient organochlorine miticide with low toxicity so that it had been promoted in tea planting cultivation. Because of a long degradation, dicofol has been banned nowadays [1]. Carbofuran is a highly toxic pesticides that forbad in tea cultivation [2]. Fenvalerate is a pyrethroid pesticide that once widely used [3] on tea cultivation. But it is mildly toxic that polluting environment so that the government prohibited it in tea cultivation. However, although these three pesticides have been banned, there are tea farmers use these pesticides in tea planting illegally. Therefore, effective detection of these banned pesticides is not only conducive to tea export trade, but also can ensure drinking people's health.

Now the main methods for the detection of pesticide residues in tea is gas chromatography [4-6] and high performance liquid chromatography [7]. In the other hand, immunoassay analysis [8], electrochemical analysis [9], enzymatic inhibition method [10], bio-sensing method [11-13], infrared spectroscopy [14, 15], fluorescence spectroscopy [16-19] are also played roles in the detection of pesticide residues. In this article, the fluorescence spectroscopy combining with 2D correlation spectroscopy is applied to analyze the characteristic parameters of pesticide residues. 2D correlation theory is expanded from narrow to broad in 1993 after repeated amendment by Noda et al [20-22]. It is to say that, the simple sine wave, pulse wave, random noise or physical changes and so on can act as perturbation. Therefore, the application of 2D correlation spectroscopy has gradually expanded to near-infrared, Raman and fluorescence spectroscopy and other techniques.

2. Experimental Methods

2.1 Instrument

Fluorescence spectrum are obtained by RF-5301PC fluorescence spectrophotometer (Shimadzu Corporation). The instrument has the 150W Xenon lamp and a 1cm cuvette adaptation. The excitation and emission slits were set to 5nm. The main technical indicators are as following: slit Range 1.5-20 nm, measurement wavelength range 220-750 nm, wavelength scan range 220-900 nm, wavelength of the velocity of approximately 20000 nm/min, wavelength accuracy (1.5 nm), letter noise ratio(150:1), grating (blazed holographic grating with F2.5 engraved lines 1300 line/mm).

2.2 Samples

Experimental pesticide samples (dicofol, carbofuran, fenvalerate) are from Jiangsu Academy of Agricultural Sciences and tea samples from a large supermarket.

2.3 Principle

2.3.1 Synchronous Spectrum

The synchronous spectrum gives information about spectral features that change in phase (i.e., occur at the same time). The peaks along the central diagonal are termed auto peaks, because they are the auto-correlation for each resolution element. The values along the diagonal are proportional to the variance of the absorbance at a given resolution element. The values above or below the central diagonal are the cross-correlation between absorbance at two different resolution elements (i.e., cm^{-1}). These values are proportional to covariance between the absorbance at the two different resolution elements. Note that $\Phi(\upsilon x, \upsilon y) = \Phi(\upsilon y, \upsilon x)$. The peaks that arise off the diagonal are referred to as cross-peaks and may have both positive and negative values. Positive cross-peaks occur for spectral features that change in phase (i.e., increase or decrease at the same time). Negative peaks arise from peaks that are correlated, but change 180° out of phase. In other words, one peak increases with respect to time, while the other peak decreases. The synchronous spectrum is symmetric about the diagonal and resembles a graphical presentation of a multivariate covariance calculation. The synchronous 2D spectra are measures of covariance.

2.3.2 Asynchronous Spectrum

The asynchronous spectrum resembles the synchronous spectrum, however it indicates covariances that occur 90° out of phase (i.e., measure changes in spectral features that vary independently). The values along the diagonal of the asynchronous 2D spectrum are zero. This trait is not surprising because the auto-correlation of a sinusoidal function with a 90° phase shift or lag will be zero. The asynchronous spectrum allows second order temporal features to be detected. A spectral feature that increases and decreases with respect to a second feature that slowly increases, might be undetected in the synchronous spectrum. However, this correlation will appear in the asynchronous spectrum. The asynchronous spectrum is anti-symmetric in that the sign changes for the values at the

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transpose matrix position Ψ (υ x, υ y)=−Ψ (υ y, υ x). This property arises because the imaginary component has properties of an odd function. In addition, the arc tangent of the ratio of the peak intensities of the asynchronous and synchronous spectra gives the phase angle between the two events. A positive phase angle indicates that the feature associated with symbol υ y lags behind in rate with the feature associated with symbol υ x. Negative phase angles indicate the opposite temporal relationship [23, 24].

3. Results and Discussion

3.1 2D Correlation Spectrum of Dicofol with Perturbation of Excitation Wavelength

In synchronous spectrum as shown in Fig. 1, auto-correlation peaks at (297, 297), (317, 317), (322, 322) and (332, 332) are positive. There are five cross peaks at (332, 322), (332, 297), (322, 297) (375, 332) and (375, 322), the front three of which are positive and the others are negative. The presence of five cross peaks instruct that peaks at 297 nm, 322 nm, 332 nm and 375 nm share a common mechanism and origin, which means all of them belong to the same substance's (dicofol) fluorescent characteristics. However, peak at 375 nm is not simultaneous with the other four peaks. With the change of the excitation wavelength (from 220 nm to 283 nm), the peaks of 322 nm and 332 nm decrease and the peak of 375 nm increases.

In asynchronous spectrum as shown in Fig. 2, there are three cross peaks, wherein (375, 332) (375, 322) are negative and (358, 317) is positive. Cross-peak at (375, 332) and (375, 322) is negative illustrating that the intensity changes of 322 nm and 332 nm happen significantly before the change of 375 nm. According to the relevant rules of the 2D correlation spectrum, the value that synchronous intensity $\Phi(\nu 1, \nu 2)$ multiplying by asynchronous intensity $\Psi(\nu 1, \nu 2)$ is negative declaring that the fluorescence intensity of $\nu 2$ changes faster than that of $\nu 1$. As a result, combining with synchronous spectrum Fig. 1, the intensty of 375 nm changes faster than that of 322 nm and 332 nm.

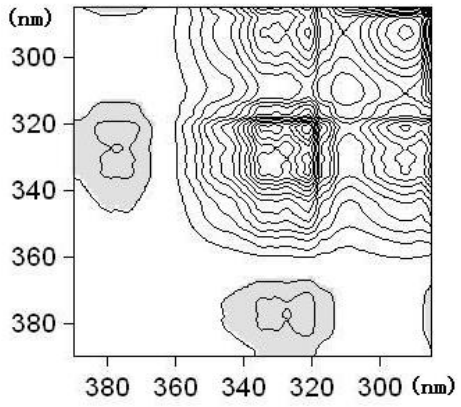

Fig. 1 Synchronous spectra of dicofol with Perturbation of excitation wavelength

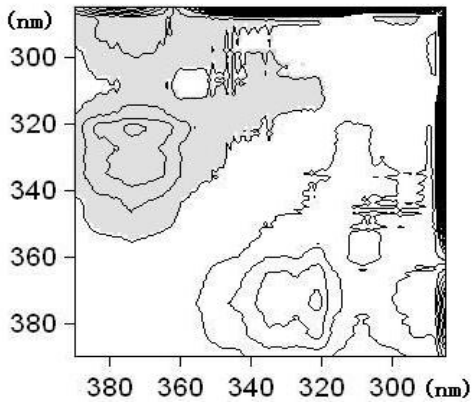

Fig. 2 Asynchronous spectra of dicofol with perturbation of excitation wavelength

Table 1 The signal peaks of dicofol in 2D correlation spectrum with perturbation of wavelength

Synchronous spectra		Asynchronous spectra
Auto-correlation peak (nm)	Cross peak (nm)	Cross peak (nm)
(297,297) (+)	(332,322) (+)	(375,332) (-)
(317,317) (+)	(332,297) (+)	(375,322) (-)
(322,322) (+)	(322,297) (+)	(58,317) (+)
(332,332) (+)	(375,332) (-)	
	(375,322) (-)	

4.2 2D Correlation Spectrum of Dicofol with Perturbation of Concentration

In synchronous spectrum shown in Fig. 3, there are four auto-correlation peaks located at (297, 297) (317, 317) (322, 322) (332, 332) and two cross peaks located at (322, 297) (332, 297). All of the auto-correlation peaks and cross peaks are positive. The presence of cross-peak (322, 297) and (332, 297) states that the mechanism and origin of 322 nm, 332 nm and 297 nm are same so that they are derived from dicofol. In addition, because of the value of the two cross peak positive, the fluorescence intensity of 322 nm, 332 nm and 297 nm change simultaneously when the concentration of dicofol changes. On the other hand, although four auto-correlation peaks appear in Fig. 3, 317nm is different from the other three because that there is no cross peaks about 317 nm and the other three (297 nm, 322 nm, 332 nm), which indicating that 317 nm belongs to a different material. It is known that 317 nm is attributed to catechin's fluorescence characteristics. In the asynchronous spectrum shown in Fig. 4, there are two cross-peaks (332, 297) and (322, 297), both of which are negative. Therefore, with perturbation of concentration, the fluorescence intensity of 297 nm changes faster than 322 nm and 332 nm.

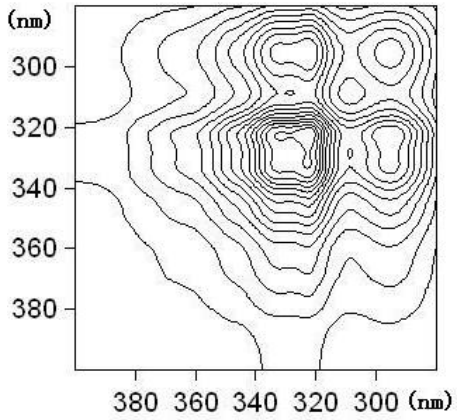

Fig. 3 Synchronous spectra of dicofol with Perturbation of concentration

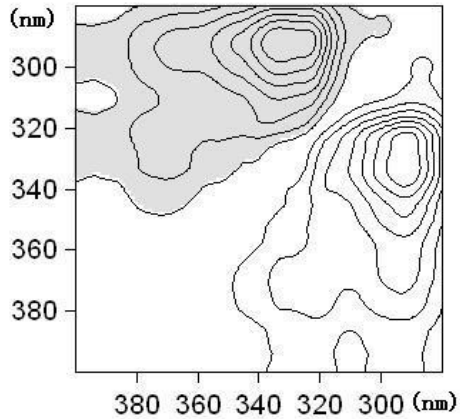

Fig. 4 Asynchronous spectra of dicofol with perturbation of concentration

Table 2 The signal peaks of dicofol in 2D correlation spectrum with perturbation of concentration

Synchronous spectra		Asynchronous spectra
Auto-correlation peak (nm)	Cross peak (nm)	Cross peak (nm)
(297,297) (+)	(322,297) (+)	(322,297) (-)
(317,317) (+)	(332,297) (+)	(332,297) (-)
(322,322) (+)		
(332,332) (+)		

4.3 2D Correlation Spectrum of Carbofuran with Perturbation of Concentration

In synchronous spectrum shown in Fig. 5, two auto-correlation peaks at (375, 375) and (297, 297) locate in the diagonal line and both of them are positive. One cross-peak at (375, 297) which is positive appears in Fig. 5. The existence of the cross peak states that 297 nm and 375 nm have a same origin, that is to say they belong to the same substance's (carbofuran) fluorescence characteristics.

In asynchronous spectrum shown in Fig. 6, there are four cross peaks at (375, 365) (375, 340) (375, 315) and (375, 297). The Cross-peaks are negative indicating that the intensity change of 365nm, 340nm, 315nm and 297 nm are significantly before the intensity change of 375 nm. In addition, combining with the synchronous spectrum Fig. 5, it is found that the change of 375 nm is faster than the change of 365 nm, 340 nm, 315 nm and 297 nm.

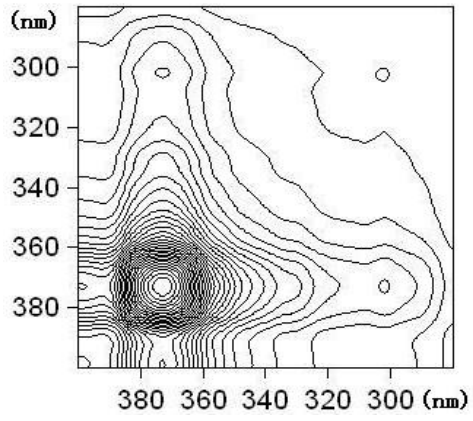

Fig. 5 Synchronous spectra of carbofuran with perturbation of concentration

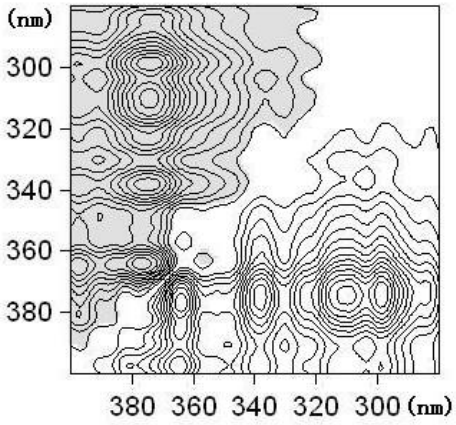

Fig. 6 Asynchronous spectra of carbofuran with perturbation of concentration

Table 3 Signal peaks of carbofuran in 2D correlation spectrum with perturbation of concentration

Synchronous spectra		Asynchronous spectra
Auto-correlation peak (nm)	Cross peak (nm)	Cross peak (nm)
(375,375) (+)	(375,300) (+)	(375,365) (-)
(300,300) (+)		(375,340) (-)
		(375,315) (-)
		(375,297) (-)

4.4 2D Correlation Spectrum of Fenvalerate with Perturbation of Concentration

In synchronous spectrum shown in Fig. 7, only one positive auto-correlation peak (375, 375) appears and there is no cross-peak. The peak 375 nm is attributed to the fluorescence characteristics of fenvalerate.

In asynchronous spectrum shown in Fig. 8, there are four cross peaks at (375, 295) (375, 315) (375, 340) (385, 375), wherein the front two peaks (375, 315) and (385, 375) are positive and the other two peaks (375, 295) and (375, 340) are negative. The existence of two positive cross-peaks, indicating the change of 375 nm is significantly before 315 nm and the change of 385 nm is significantly before 375 nm. The presence of two negative cross-peaks, indicating the light intensity change significantly before 295 nm 375 nm, 340 nm light intensity change significantly before 375 nm. Combining with synchronous spectrum Fig. 7, it is seen that the intensity of 375 nm changes faster than 315 nm and the intensity of 385 nm changes faster than 375 nm. Besides both intensities of 295 nm and 340 nm change faster than 375 nm.

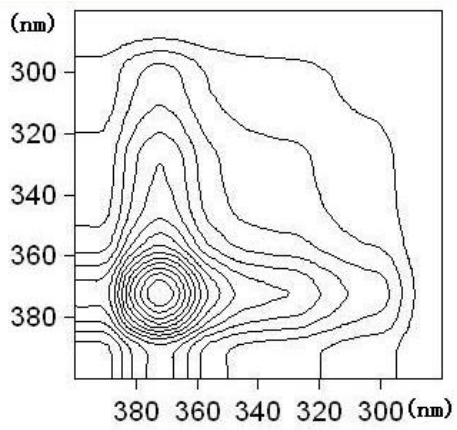

Fig. 7 Synchronous spectra of fenvalerate With perturbation of concentration

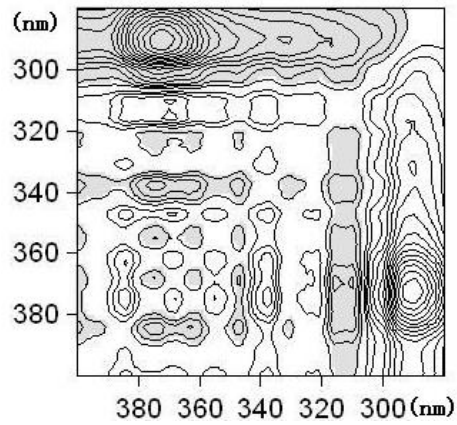

Fig. 8 Asynchronous spectra of fencalerate with perturbation of concentration

Table 4 Signal peaks of fenvalerate in 2D correlation spectra with perturbation of concentration

Synchronous spectra	Asynchronous spectra
Auto-correlation peak (nm)	Cross peak (nm)
(375,375) (+)	(375,295) (-)
	(375,315) (+)
	(375,340) (-)
	(385,375) (+)

Table 5 The feature extraction of 2D correlation spectrum of dicofol, carbofuran and fenvalerate

Perturbation	Dicofol				Cabofuran		fenvalerate	
	wavelength		concentration		concentration		concentration	
	Synchronous	Asynchronous	Synchronous	Asynchronous	Synchronous	Asynchronous	Synchronous	Asynchronous
Mean value	3424	-6.55×10^{-14}	849.3	5.637×10^{-15}	192.2	-3.34×10^{-16}	141.7	-4.11×10^{-15}
Standard deviation	3643	1631.6	514.51	74.27	139.42	7.526	946.6	27.003
Center of gravity (nm,nm)	354.4, 354.4	354.2, 354.2	352.5, 352.5	374.9, 374.9	319.5, 319.5	361.8, 361.8	323.8, 323.8	377.5, 377.5
Skewness	-0.212	3.1411	0.3203	-0.9082	0.8233	0.3411	0.6306	-1.3598
Kurtosis	1.681	13.849	2.038	2.2	2.399	1.692	2.675	3.653
Consistency	0.549	0.499	1	0.483	1	0.435	1	0.479
Entropy	0.93	1.01	-3.3×10^{-16}	1.231	-3.3×10^{-16}	-3.33×10^{-16}	-3.3×10^{-16}	1.289

4.5 The Feature Extraction of 2D Correlation Spectrum of Dicofol, Carbofuran and Fenvalerate

Based on Matlab, the statistical characteristics such as mean value, standard deviation, the center of gravity, standard deviation, standard deviation of the wavelength domain, skewness, kurtosis, consistency and entropy are extracted. These features reflect the distibution of 2D correlation spectra of each pesticide with a clear sense of macroscopic geometry.

4. Conclusion

In this paper, the characteristics of 2D correlation spectrum of three banned pesticides in tea are studied. For the signal peaks in spectral characteristics, with perturbation of excitation wavelength, there are four auto-correlation peaks and five cross-peaks in the synchronous spectra of dicofol and three cross-peaks in the asynchronous spectra of dicofol. With perturbation of concentration, the synchronous spectra of dicofol has four auto-correlation peaks and two cross-peaks and the asynchronous spectra of dicofol has two cross-peaks. So with different perturbation, signal peaks of 2D correlation spectrum of a substance are different. In addition, with perturbation of concentration, the synchronous spectra of carbofuran has two auto-correlation peaks and one cross-peak and the asynchronous spectra of carbofuran has four cross-peaks. While the synchronous spectra of fenvalerate has one auto-correlation peak and the asynchronous spectra of carbofuran has four cross-peaks. It is can be seen that with the same perturbation, different substance has different 2D correlation spectra though the fluorescence spectrum of them are similar. Moreover, the statistical characteristic parameters such as mean value,standard deviation, the center of gravity, standard deviation, standard deviation of the wavelength domain, skewness, kurtosis, consistency, entropy are calculated using MATLAB for each 2D correlation spectra. In a word, the investigation of characteristics of 2D correlation spectrum of pesticides in tea provide the basis for species identification of pesticides.

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References

[1] E.H. Li, M. Hu, B.B. Wu, Determination of residues of dicofol and pyridaben in tea by gas chromatography, Mod. Agrochem. 5 (2006) 20-21.

[2] L. Gu, L. Ding, Study on determination of carbamate material in tea by liquid chromatography, Mod. Agr. Sci. Technol. 15 (2012) 286-291.

[3] X.Y. Wu, Y.D. Yue, G.S. Huang, Dissipation behavior of fenvalerate residue in made tea during brewing process and its maximum residues levels evaluation, Acta Laser Biol. Sin. 16 (2007) 469-474.

[4] F.B. Tang, Z.M. Chen, F.J. Luo, Determination of organophosphorus pesticide residues in tea by solid-phase extraction-gas chromatography, Chin. J. Anal. Lab. 26 (2007) 43-47.

[5] G.M. Hao, H.X. Li, C.J. Zhao, Determination of organochlorine pesticide residues in tea by gas chromatography, Food Sci. 11 (2001) 73-75.

[6] Z.Q. Huang, Y.J. Li, B. Chen, Simultaneous determination of 102 pesticide residues in chinese teas by gas chromatography-mass spectrometry, J. Chromatogr. B 853 (2007) 154-162.

[7] W. Xie, Y. Qian, H.Y. Ding, Determination of six neonicotinoid pesticides residues in tea samples using high performance liquid chromatography tandem mass spectrometry, Chinese J. Anal. Chem. 37 (2009) 495-499.

[8] Y.J. Yang, Y.Wang, X.R. Yang, Application of immunoassay analysis in doing test of pesticide residues, Acta Agr. Boreali-sin. 16 (2001) 119-114.

[9] [9]S. Du, G.D. Jin, X.Y. Hu. Indirect Determination of acetamiprid by the electrochemical method. J. Instru. Anal. 29(2010) 331-335.

[10] J.Z. Zhao, Z.J. Fan, Z.Y. Wang, Examination of the pesticide residue of organophosphates and carbarnates on the spot by thin-layer chromatography-enzyme inhibition method, J. Sichuan Norm. Uni. (Nat. Sci.) 24 (2001) 496-498.

[11] C. Dong, Y.M. Shi, L.P. Zhang, Investigation of pesticide residues by the plant esterase, Meth. Pestic. 40 (2001) 19-20.

[12] Z.H. Xie, The research and application of new nanomaterials in enzyme, Biosensor, Shanghai, East China normal University, China, 2007.

[13] H.L. Gao, T.F. Kang, X.Q. Wang, Determination of organophosphrus pesticides using a biosensor of acetylcholinesterase mobilized by sol-gel method, Environ. Chem. 24 (2005) 707-710.

[14] R.J. Dijkstra, F. Ariese, C. Gooijier, U.A. Brinkman, The Raman spectroscopy as a detection method for liquid-separation techniques, TrAC Trendsin Anal. Chem. 24 (2005) 304-323.

[15] Y.A. Woo, H.J. Kim, J.H. Cho, Discrimination of herbal medicines accordiing to geographical origin with near infrared refledtance spectroscopy and pattern recognition techniques, J. Pharmaceut. Biomed. Anal. 24 (2001) 407- 413.

[16] L.L. Li, W.J. Yu, W.E. Liu, Rapid fluorimetic detemination of organophosphorus pesticides, Liaoning Agricul. Sci. 7 (2001) 24-25.

[17] R.S. Che, S.T. Wang, Study of fiber fluorescence spectrometer for monitoring carbamate imidacloprid insecticide, J. Optoelectron. Laser. 15 (2004) 541-544.

[18] S. Hassoon, I. Schechter, In situ fluorimetric determination of pesticides on vegetables, Anal. Chim. Acta. 405 (2000) 9-15.

[19] Z.D. Wang, Y.T. Wang, X.J. Guan. Study on the fluorescence characteristic for carbamate pesticides, Anal. Test. Technol. Instru. 10 (2004) 214-217.

[20] I. Noda, Advances in two-dimensional correlation spectroscopy, Vibr. Spectrosc. 36 (2004) 143-165.

[21] I. Noda, Two-dimensional infrared (2D IR) spectroscopy: theory and applications, Appl. Spectrosc. 44 (1990) 550-561.

[22] I. Noda, Generalized two-dimensional correlation methods applicable to infrared, Raman and other types of spectroscopy, Appl. Spectrosc. 47 (1993) 1329-1336.

[23] M. Lei, X.H. Feng, The generalized two-dimensional correlation spectroscopy technology and its applies, Chin. J Spectrosc. Lab. 25 (2008) 996-1002.

[24] T.P. Jandler, P.D. Harrington, H. Richardson, Effects of static spectrum removal and noise on 2D-correlation spedtra of kinetic data, Anal. Chim. Acta. 368 (1998) 45-57.