

Ratio Derivative Spectroscopic Analysis of Thiamethoxam Residue in Tea

Jihua Zhang¹, Zhimin Zhao^{1,*}, Lexin Wang¹

1.College of Science, Nanjing University of Aeronautics and Astronautics

Nanjing, 210016, China

Abstract

In this paper, ratio derivative UV spectroscopic method was developed and validated for the determination of thiamethoxam residue in tea. To estimate thiamethoxam, the amplitude of the first derivative of the corresponding ratio spectra at 258nm was used. Correlation coefficient of the calibration model was considered to be 0.9977. Besides the method was validated according to ICH guidelines by assessing the linearity, accuracy, limit of quantification, limit of detection. The results demonstrate that ratio derivative spectrophotometry is suitably applied for the detection of thiamethoxam residue in tea.

I. INSTRUCTION

Thiamethoxam, a novel broad-spectrum insecticide with low toxicity, is a second-generation neonicotinoid insecticide, whose mechanism of action is similar to the first-generation neonicotinoid imidacloprid but with higher activity. It has good control to sucking pests such as aphids, planthoppers, leafhoppers, whiteflies, etc[1]. As thiamethoxam is widely used in tea production in recent years, the EU requires to detect residues of thiamethoxam when China's tea exports to the EU. Due to the complexity components of the tea sample, it is necessary to build an efficient, fast and simple analytical method of triumphant residues. The current mainly method for detecting residues of thiamethoxam is gas chromatography and high performance liquid chromatography[2-6].

In the early 1990s, F.Salinas etc.[7] developed a new method called "ratio-derivative Spectrophotometry" based on the linear regression analysis of multi-wavelength and derivative spectrophotometric

analysis. This method can eliminate low-frequency background noise and has strong distinguishability[8]. At the same time, good sensitivity and accuracy make it to bring out less error when improving resolution.

Application of this method, Salinas[7] determined salicylic acid and salicylic acids at 241.5nm and 247nm respectively at the same time and the recoveries were in a range of 95%-108%. In addition, the method was widely used in drugs[9,10], food additives[11-15], environmental water[16,17] and so on. The basic principles of ratio derivative spectroscopy is as following:

According to Beer's law, the absorbance of the mixture of a and b can be described as:

$$A_{a+b,\lambda} = A_{a,\lambda} + A_{b,\lambda} = c_a \varepsilon_{a,\lambda} + c_b \varepsilon_{b,\lambda}$$

Wherein, $A_{a+b,\lambda}$ is the absorbance of the mixture

components of a, b at wavelength λ ; $\varepsilon_{a,\lambda}$ and $\varepsilon_{b,\lambda}$ is

the Absorption coefficient respectively, c_a and c_b

is the concentration of component a and b, respectively.

The ratio spectrum can be obtained by dividing the

standard spectra of the b component $A_{b,\lambda}^0$

$$\frac{A_{a+b,\lambda}}{A_{b,\lambda}^0} = \frac{c_a}{c_b} \frac{\varepsilon_{a,\lambda}}{\varepsilon_{b,\lambda}} + \frac{c_b}{c_a}$$

And then the first derivative with respect to λ has been done on both sides of the equation:

$$\frac{d}{d\lambda} \left[\frac{A_{a+b,\lambda}}{A_{b,\lambda}^0} \right] = \frac{c_a}{c_b} \frac{d}{d\lambda} \left[\frac{\varepsilon_{a,\lambda}}{\varepsilon_{b,\lambda}} \right]$$

The above equation indicates the ratio derivative absorbance is independent of concentration of component b. Obviously, the ratio derivative

absorbance $\left(\frac{d}{d\lambda} \left[\frac{A_{a+b,\lambda}}{A_{b,\lambda}^0} \right] \right)$ can be used for

quantitative analysis of component a.

II. EXPERIMENTAL

A. Instruments and Samples

Shimadzu UV-3600 UV-visible absorption spectrometer is used. It consists of a light source, a monochromator, an absorption cell, a detector and a data system components. It is under a resolution of 0.1nm. Stray light is 0.00008% T or less and the measurement wavelength range is 185-3300nm.

Thiamethoxam, content of effective constituent of 96%. Tea, purchased in the market, is brewed by boiling water in 10min and stewing to get supernate. Then thiamethoxam is dissolved in the supernate to obtain the concentration in Table I.

III. RESULTS AND DISCUSSION

A. Ratio First Derivative Spectrophotometry

Figure 1 shows the ratio spectra of different concentrations of thiamethoxam (spectra divided by the spectrum of tea) while Figure 2 shows their first derivatives. As it can be seen, there are a peak at 243nm and a valley at 258nm in the ratio derivative spectra corresponding to thiamethoxam residue in tea. So the amplitude of the two wavelengths are selected for quantitative determination of thiamethoxam in tea.

B. Validation

1) Linearity and Range

The calibration graphs for the determination of thiamethoxam residue in tea were constructed by plotting the derivative absorbance versus the concentrations as shown in Figures 3 and 4. The graphs were found to be rectilinear over the concentration ranges cited in Table II.

2) Statistical Analysis

Statistical analysis of the data gave high value correlation coefficients (r) of the regression

equations, small values of the standard deviations of residuals (Sy/x), of intercept (Sa), and of slope (Sb), and small values of percentage relative standard deviation and percentage relative error (Table II). These data proved the linearity of the calibration graphs and the agreement of the results of Beer's law. However, y/x, Sa and Sb of 243nm are almost twice than those of 258nm which indicate that the indeterminacy of 243nm is higher than 258nm.

3) Accuracy

Relative standard deviation (RSD) and the percentage relative error can usually be used to represent the precision. The RSD of 258nm is 0.99% rather the RSD of 243nm is 1.23% and the percentage relative error of 258nm is smaller than that of 243nm, clarifying the precision of 258nm is extremely higher.

3.2.4 Limit of Detection (LOD) and Limit of Quantitation (LOQ) The limit of quantification (LOQ) was determined by establishing the lowest concentration that can be measured [18] below which the calibration graph is non linear while the limit of detection (LOD) was determined by evaluating the lowest concentration of the analyte that can be readily detected. The results are shown in Table II. LOD and LOQ were calculated according to the following equations: [18]

$$\text{LOQ} = 10S_a/b;$$

$$\text{LOD} = 3.3S_a/b;$$

Where Sa is the standard deviation of the intercept of regression line, and b is the slope of the calibration curve.

According to the result shown in Table II, 258nm is more suitable for the determination of thiamethoxam residue in tea.

C. Prediction

In order to obtain the prediction of the calibration model shown in section 4.2, the concentrations of the samples in the test set are predicted, shown in Table III. As to be seen, the average recovery is 103.8% and the average prediction error is $0.036 \times 1/120$ mg/mL, which stating the calibration model can predict the

concentration of thiamethoxam in tea. Therefore, the ratio derivative spectrophotometric analysis is an effective and exact method for the detection of thiamethoxam in tea.

IV. CONCLUSION

The ratio derivative spectroscopic method could be utilized for the detection and determination of thiamethoxam residue in tea. There are a peak at 243nm and a valley at 258nm in the ratio derivative spectra of thiamethoxam. However, the calibration result of 258nm was better than the calibration result of 243nm according to their correlation coefficient, Standard deviation of the residuals Sy/x , Standard deviation of the intercept, Standard deviation of the slope, Limit of detection (LOD) and Limit of quantification (LOQ). Hence 258nm was supposed to be the research wavelength for the calibration. The prediction showed the calibration model of 258nm could predict the concentration of thiamethoxam in tea. Therefore, the ratio derivative spectroscopic method is a simple, economical, rapid, accurate method for the determination of thiamethoxam in tea.

ACKNOWLEDGMENTS

This work is supported by Program sponsored for scientific innovation research of college graduate in Jiangsu province (CX13_146), Funding for Outstanding Doctoral Dissertation in NUAA (BCXJ13-15), the National Natural Science Foundation of China (NO.10172043).

REFERENCES

[1] Xianfeng Wang. Imported Pesticide Application Manual. (China Agriculture Press, Beijing, 2000) Pp. 209-210.
 [2] Singh S B, Foster G D, Khan S U. J Agr Food Chem , 52: 105-109(2004).

[3] Campbell, Chen S, Yull. J Agr Food Chem , 53: 5373-5376(2005).
 [4] Wei Li, Guoguang Liu, Liqing Zheng. J. Agro-Environ. Sci. 26: 739-742(2007).
 [5] Zhengyun Lou, Fubin Tang, Zongmao Chen. Chinese J Anal Lab, 28: 76-78(2009).
 [6] Wen Xie, Yan Qian, Huiying Ding. Chinese J Anal Chem, 37: 495-499(2009).
 [7] F.Salinas, J.J.Berzas Nevado and A.EsPinoso Mansilla. Talanta, 37:347-351(1990).
 [8] Morelli B. Anal Lett, 27:2751(1994).
 [9] Berzas Nevado, J.J., Rodriguez Flores, J.:De la Morena Pardo M. L. Analisis, 21:33-37(1993).
 [10] Erdal Dinc, Feyyaz Onur. Chim Acta, 359:93-106(1998).
 [11] Berzas Nevado, J.J., Rodriguez Flores, J., Villasenor Lleren, M.J.. Analisis, 21:395-401(1993).
 [12] Berzas Nevado, J.J., Lemus Gallego, J.M., Castaneda Penalvo, G. Quim. Anal.(Barcelona), 13:42-46(1994).
 [13] Berzas Nevado, J.J., Rodriguez Flores, J., VillasenorLleren, M.J.. Talanta, 40:1391-1396(1993).
 [14] Berzas Nevado, J.J., Rodriguez Flores, J., VillasenorLleren, M.J.. Anal.Lett, 27:1009-1029(1994).
 [15] Zhiyong Huang, Haitao Lai, Xiaojing Zhang. Food Ferment Ind, 27:50-53(2001).
 [16] Shaoqian Liu, Jinwu Mao, Shaogang Liu. Bull Hunan Med Uni, 25:87-89(2000).
 [17] Berzas Nevado, J.J., Rodriguez Flores, J., De la Morena Pardo, M.L.. Talanta, 38:1261-1264(1991).
 [18] ICH Harmonized Tripartite Guideline Validation of Analytical Procedures:Text and Methodology, Q2(R1), Current Step 4 Version, Parent Guidelines on Methodology Dated November 6, 1996, Incorporated in November 2005, (accessed February 28, 2008)

Figure captions

- Fig 1 The ratio spectrum of thiamethoxam (the UV spectra of tea as divisor)
 Fig 2 The ratio derivative spectrum of thiamethoxam
 Fig 3 The calibration model of 243nm
 Fig 4 The calibration model of 258nm

Table I Concentrations of Thiamethoxam In Tea Water

Calibration set		Test set	
samples	concentration (mg/mL)	samples	concentration (mg/mL)
a	1 × 1/120	A	1.5 × 1/120
b	2 × 1/120	B	2.5 × 1/120
c	3 × 1/120	C	3.5 × 1/120
d	4 × 1/120	D	4.5 × 1/120
e	5 × 1/120		

Table II The Calibration Models of 258nm and 243nm

Parameter	Ratio derivative method	Ratio derivative method
	258nm	243nm
Wavelength (nm)	258nm	243nm
Concentration range (1/120 mg/mL)	1-5	1-5
Intercept (a)	-1.61×10^{-3}	2.51×10^{-3}
Slope (b)	0.01497	0.0178
Correlation coefficient (r)	0.9977	0.98569
Standard deviation of the residuals Sy/x	1.39×10^{-4}	2.93×10^{-4}
Standard deviation of the intercept, Sa	3.75×10^{-4}	7.94×10^{-4}
Standard deviation of the slope, Sb	1.13×10^{-4}	2.39×10^{-4}
Relative standard deviation, RSD(%)	0.99	1.23
Percentage relative error, Error(%)	0.77	0.95
Limit of detection (LOD) (1/120 mg/mL)	0.083	0.15
Limit of quantitation (LOQ) (1/120 mg/mL)	0.25	0.45

Table III The Prediction Result of the Calibration model of 258nm

sample	Reference (1/120mg/mL)	Prediction (1/120mg/mL)	Recovery (%)	Error (1/120mg/mL)
A	1.5	1.695	113.0	0.195
B	2.5	2.779	111.2	0.279
C	3.5	3.214	91.83	-0.286
D	4.5	4.458	99.07	-0.042

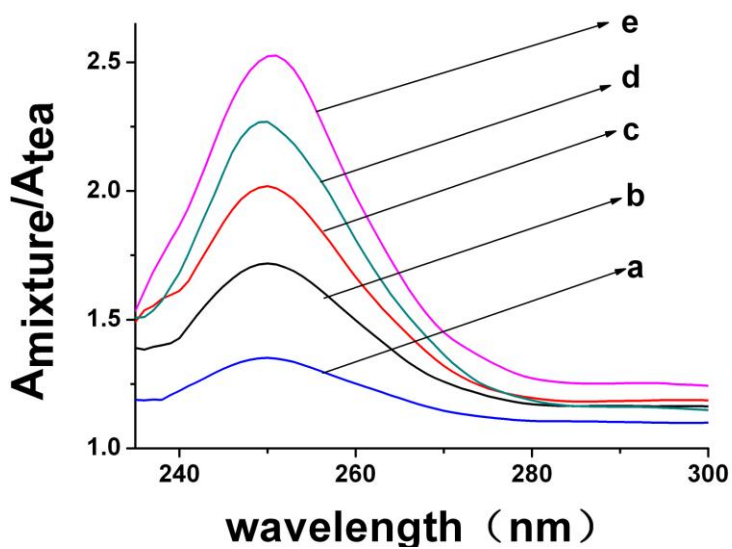


Fig 1

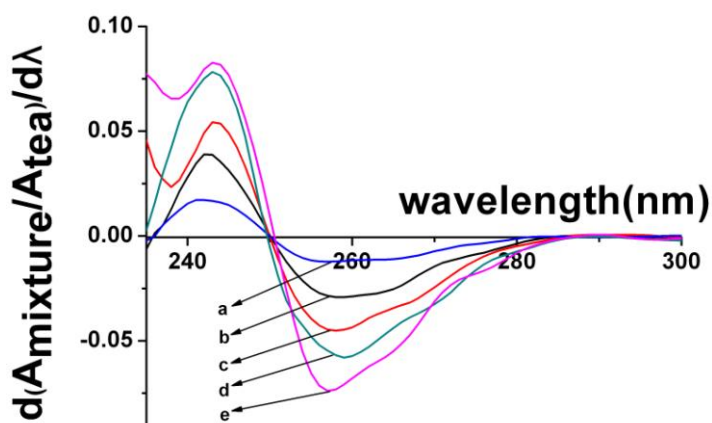


Fig 2

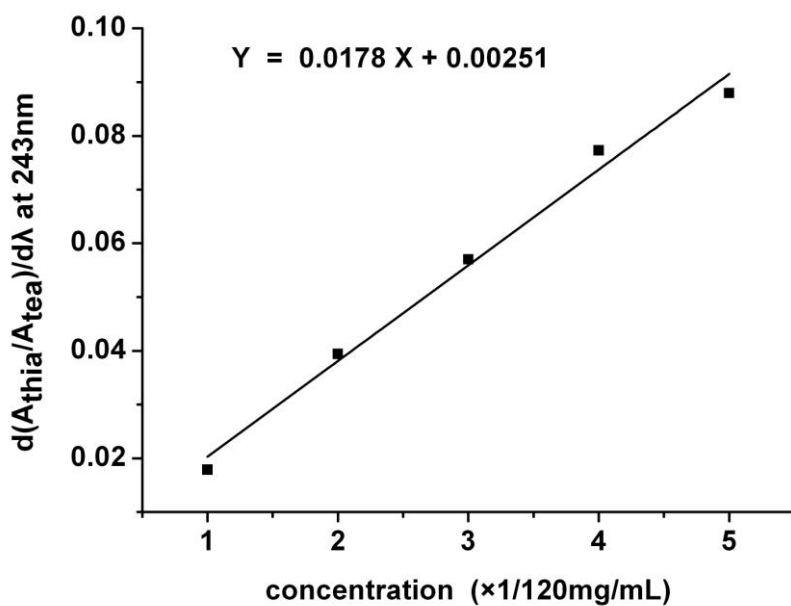


Fig 3

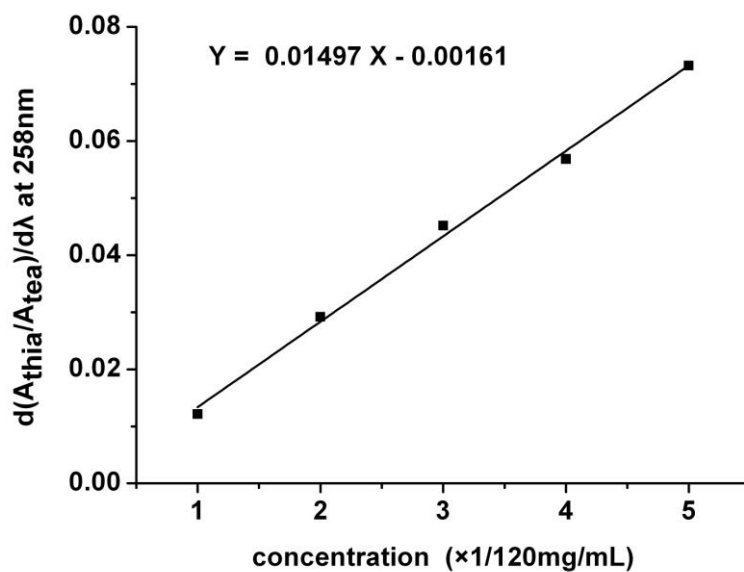


Fig 4