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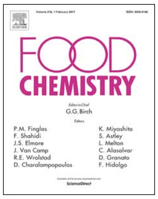

Analytical Methods

An effective approach to quantitative analysis of ternary amino acids in foxtail millet substrate based on terahertz spectroscopy

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ABSTRACT

Terahertz time-domain spectroscopy has been applied to many fields, however, it still encounters drawbacks in multicomponent mixtures analysis due to serious spectral overlapping. Here, an effective approach to quantitative analysis was proposed, and applied on the determination of the ternary amino acids in foxtail millet substrate. Utilizing three parameters derived from the THz-TDS, the images were constructed and the Tchebichef image moments were used to extract the information of target components. Then the quantitative models were obtained by stepwise regression. The correlation coefficients of leave-one-out cross-validation (R^2_{loo-cv}) were more than 0.9595. As for external test set, the predictive correlation coefficients (R^2_p) were more than 0.8026 and the root mean square error of prediction ($RMSE_p$) were less than 1.2601. Compared with the traditional methods (PLS and *N*-PLS methods), our approach is more accurate, robust and reliable, and can be a potential excellent approach to quantify multicomponent with THz-TDS spectroscopy.

1. Introduction

Terahertz spectroscopy is a newly mentioned technology, ranging from 0.1 to 10 THz (1 THz = 10^{12} Hz) and locating between the microwave and infrared regions in the electromagnetic spectrum. Owing to its low power and radiation, no light ionization and damage (Fitzgerald et al., 2002), it is safe to the bio-molecules with THz wave (Baxter & Guglietta, 2011). Non-destructive detection and screening have been done using terahertz time-domain spectroscopy (THz-TDS) technique where spectral absorptions in THz region were obtained, such as for DNA (Markelz, Roitberg, & Heilweil, 2000), amino acids and proteins(Lu, Zhang, Zhang, Yang, & Xiang, 2016; Ueno, Rungsawang, Tomita, & Ajito, 2006), crystalline samples (Shibata, Mori, & Kojima, 2015), pesticides (Chen et al., 2015) and diagnosis of cervical cancer (Qi, Zhang, Xiang, Yang, & Harrington, 2015). These articles only focused on the absorption coefficient in the quantification. Actually, the absorption coefficient and the other two parameters (extinction coefficient and refractive index) can be calculated from THz spectra at the same time, which are always used as calculating auxiliary means to discuss the intermolecular vibrational modes of the complexes (Yamamoto, Kabir, Hayashi, & Tominaga, 2005) or used as qualitative methods to distinguish biomolecules' differentiation (Yamamoto et al., 2004) and other chemical materials (Hu et al., 2005). In our opinion, these three parameters contain the different information of samples, and their fusion will provide more information of the samples for quantitative analysis.

As one of the most vital drought-resistant crops, millet is also the crucial source of world's food, which is widely grown in the arid and semiarid areas of Africa and Asia, and it is the main source of carbohydrates and proteins to the people living in those regions (Saleh, Zhang, Chen, & Shen, 2013). For example, foxtail millet (*Setaria italica*) is widely grown in northern China and commonly used as a nourishing gruel or soup for pregnant and nursing women (Mohamed, Zhu, Issoufou, Fatmata, & Zhou, 2009). Foxtail millet has also been utilized as a Chinese traditional medicine to recuperate kidney's energy, regulate the damp heat of spleen and stomach, cure the excessive thirst and make convenient urination according to the "Compendium of Materia Medica". Recently more foxtail millet products such as millet porridge, millet wine, and millet nutrition powder have entered into our daily lives and its cultivation zones have also increased worldwide (Yang et al., 2013). The determination of the components in foxtail millet has become a vital part of production and quality control. Since millets typically contain higher quantities of essential amino acids than maize, rice, and sorghum (Obilana & Manyasa, 2002) and amino acids have been measured by diverse spectroscopic systems (Jenkins, Larsen, & Williams, 2005; Matei, Drichko, Gompf, & Dressel, 2005), however, reference techniques are complex, expensive, time-consuming and can also damage the specimen (Gaillard, Trivella, Stote, & Hellwig, 2015;

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Table 1
The experimental (Exp.) and calculated (Cal.) concentrations of the three amino acids in yellow foxtail millet.

Datasets	Sample No.	Gln				Glu				Tyr			
		Exp.	Cal.			Exp.	Cal.			Exp.	Cal.		
			TM	N-PLS	PLS		TM	N-PLS	PLS		TM	N-PLS	PLS
Calibration set	1	3.27	2.55	3.76	2.39	0	0.49	0.70	0.01	0	−0.52	−0.54	−0.07
	2	13.13	13.20	12.31	13.19	0	0.05	−0.15	0.07	0	−0.12	−0.05	−0.15
	3	0	0.49	0.45	0.44	3.34	3.03	3.49	3.21	0	0.15	0.32	0.46
	4	0	−0.18	−0.45	−0.09	13.25	13.19	13.48	13.42	0	−0.15	−0.59	−0.31
	5	0	0.38	0.25	0.03	0	−0.03	0.76	0.56	3.39	3.45	3.53	3.70
	6	0	−0.28	0.06	−0.64	0	−0.10	−0.16	−0.04	13.74	13.54	13.34	13.56
	7	1.26	1.35	2.74	1.69	0.99	1.05	1.22	0.70	1.13	1.30	1.53	0.92
	8	1.06	1.04	1.71	1.45	1.00	1.23	0.87	0.85	1.06	1.46	0.91	1.11
	9	1.20	1.85	2.53	1.63	2.33	2.51	2.91	2.46	2.53	2.16	2.84	2.53
	10	1.26	2.16	1.89	1.92	2.38	1.86	2.28	2.34	2.38	1.96	2.31	1.87
	11	0.94	1.56	0.88	1.31	5.01	4.67	4.23	4.54	4.95	4.91	4.39	4.88
	12	1.26	0.32	0.80	0.52	4.99	5.28	4.98	5.02	4.86	5.19	5.06	4.81
	14	1.06	0.66	1.60	0.83	7.42	7.45	7.05	6.80	7.75	8.09	8.01	7.82
	15	2.46	2.07	3.98	2.82	1.26	1.33	1.55	1.36	2.39	2.29	2.77	2.30
	18	2.47	2.48	3.54	3.05	2.40	2.98	2.78	2.59	0.93	1.44	0.61	1.15
	19	2.25	2.41	3.33	2.60	5.36	6.31	6.11	6.10	7.42	6.89	7.23	7.30
	20	2.32	2.78	4.15	2.92	5.18	4.66	5.08	5.38	7.50	7.88	7.55	7.70
	21	2.46	2.35	1.78	2.76	7.59	7.77	7.81	7.97	5.06	5.09	5.47	5.25
	22	2.40	3.20	3.12	3.18	7.28	7.14	6.91	6.77	4.88	5.04	5.00	4.96
	23	4.97	4.67	4.70	5.16	1.19	1.35	1.64	1.43	5.17	5.66	5.43	5.01
	24	4.93	4.98	5.86	4.66	1.20	1.08	1.46	1.21	5.06	4.59	5.49	5.13
	25	5.32	5.88	6.55	5.57	2.46	2.72	2.17	2.33	7.04	7.26	6.77	7.23
	26	4.78	4.23	2.13	3.81	2.59	2.53	1.72	2.24	7.57	7.26	7.10	7.20
	28	5.13	4.13	4.43	4.17	5.27	4.81	4.87	5.05	0.93	1.34	1.63	1.35
	30	4.92	5.19	3.85	4.57	7.38	7.36	7.53	7.49	2.33	2.78	2.83	2.36
	32	7.70	8.03	8.27	8.43	1.19	0.91	0.85	1.12	7.37	7.03	6.99	7.33
	33	7.49	6.64	5.65	5.54	2.45	2.25	2.60	2.66	5.11	4.79	4.69	5.17
	36	7.29	7.40	3.75	7.17	5.17	4.88	4.48	5.36	2.45	2.55	3.19	2.79
	37	7.61	7.49	5.71	8.16	7.61	7.59	7.00	7.65	1.19	0.77	0.02	0.60
	38	7.34	7.31	8.10	7.07	7.60	7.56	8.09	7.30	1.06	1.17	1.40	1.27
Prediction set	13	1.20	−0.11	0.63	−0.30	7.65	8.06	7.18	7.06	7.31	7.61	7.51	7.78
	16	2.60	2.78	3.98	2.83	0.87	0.57	1.17	0.84	2.30	2.67	2.44	2.02
	17	2.54	3.22	3.15	3.56	2.54	1.92	2.31	2.27	1.07	1.10	1.26	0.88
	27	5.17	3.49	4.48	3.25	5.23	4.80	4.79	4.28	1.13	0.88	1.63	1.98
	29	5.04	4.27	4.16	5.04	7.75	8.12	6.75	6.87	2.39	1.84	2.22	2.39
	31	7.33	8.29	7.36	7.61	1.00	0.91	0.12	0.72	7.92	7.57	6.48	7.33
	34	7.49	5.92	7.07	6.90	2.45	2.22	3.29	3.30	4.97	3.53	7.82	6.16
	35	7.42	5.50	6.45	5.20	5.17	5.93	5.32	4.82	2.45	1.60	3.28	3.06

Exp. & Cal. are all fractional concentrations (%).

Zhu, Zhu, Fan, & Wan, 2011). Therefore, it is hopeful to introduce the non-destructive terahertz analysis as the detection technology.

Since THz spectra under study revealed linear behaviors with overlapping and complexity of signals, quantitative analyses of target components are often made by means of some chemometric methods. Partial least squares (PLS) (El Haddad et al., 2014; Ge, Jiang, Lian, Zhang, & Xia, 2016; Jiang, Ge, Lian, Zhang, & Xia, 2016; Qin, Xie, & Ying, 2014) and multivariate curve resolution alternating least squares (MCR-ALS) (Zhang, Lu, Liao, & Zhang, 2017) have been employed to the quantitative analysis of multi components based on the absorption coefficient in THz band. The results were quite satisfactory in simple systems such as polyethylene (PE) used as substrate, however, when comes to the real or complex substrate, the quantitative results are often unsatisfactory due to the serious spectral overlapping and distortions. Although the three parameters (absorption coefficient, extinction coefficient and refractive index) can be calculated simultaneously from THz spectra, the most analytical works are only based on one of the parameters, which mean that the information of samples is not fully utilized. As can be seen from the published works (Lu et al., 2016; Zhang et al., 2017), these two works were all used yellow foxtail millet as substrate instead of PE to simulate the naturally complex cereal systems. However, the results were less satisfactory when the components grew and more complicated, which may due to incomprehensive of the information or the signal overlap and baseline drift could not be handled well.

To take full advantage of the more information about samples, the three parameters calculated from THz spectra could be employed simultaneously to construct the three-dimensional (3D) spectra of samples. For the 3D spectra, several chemometric methods have been developed such as *N*-way partial least squares (*N*-PLS) (Durante, Cocchi, Grandi, Marchetti, & Bro, 2006), parallel factor analysis (PARAFAC) (Zou et al., 2009), alternating trilinear decomposition (ATLD) (Wang et al., 2014), multivariate curve resolution alternating least squares (MCR-ALS) (Azzouz & Tauler, 2008) and image processing method (Zhai, Hu, Huang, & Chen, 2010). For the determination of multi-components based on complex substrate with THz-TDS, MCR-ALS and ATLD methods were also used to deal with our 3D data set, however, the results were not satisfactory enough. They may require some necessary spectral pretreatments. Recently, Tchebichef image moment (TM) method has been applied successfully in analytical chemistry to determine multi-compounds in complex samples based on three-dimensional (3D) fingerprint spectra of HPLC (Li, Chen, Li, Wang, & Zhai, 2015), LC-MS (Xu, Li, Wang, Chen, & Zhai, 2016) and NMR(Li et al., 2017).

In this work, TM method was introduced as a novel strategy to tackle the shortcomings of THz in multicomponent mixtures analysis caused by the serious spectral overlapping and shifting displayed. Unlike the conventional quantitative analysis (only based on the