J Food Sci Technol (August 2015) 52(8):5347–5351
DOI 10.1007/s13197-014-1576-3

ORIGINAL ARTICLE

Study of the rapid detection of γ-aminobutyric acid in rice wine based on chemometrics using near infrared spectroscopy

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Revised: 5 September 2014 / Accepted: 16 September 2014 / Published online: 25 September 2014

Abstract Rice wine, in which γ-aminobutyric acid is present, is beneficial to human health and is one of the three most well-known fermented wines in the world, and is very popular in China. The rapid detection of γ-aminobutyric acid was studied in rice wine using near infrared spectroscopy with an optical fibre probe. Through the selection of detection conditions, including a waveband range of 12500–4000 cm^{-1}, a scanning duration of 16 scans and a resolution of 8 cm^{-1}, the near infrared spectrum of rice wine was acquired three times, for every wine sample, with an optical fibre probe. The resulting average value of the spectrum was obtained and the corresponding data were analysed via normalization. By adopting a multivariate calibration partial least squares method (PLS) and establishing a calibration model, the highest precision for γ-aminobutyric acid in rice wine was predicted when the factor coefficient was 17. The overall results demonstrating the content of γ-aminobutyric acid in rice wine was predicted to be between 157.6696–317.5813 mg/L, with a relative standard deviation of prediction between 0.01–5 %, as well as the fact that the single sample measuring time was less than 20 s, prove that near infrared spectroscopy is a rapid, accurate and effective method to adopt for detecting the content of γ-aminobutyric acid in rice wine.

Keywords Near infrared spectroscopy · Optical fibre probe · γ-aminobutyric acid (GABA) · Rice wine · Partial least squares

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Introduction

Rice wine, in which γ-aminobutyric acid (GABA) is present, favourably influences human health and is one of the three most well-known fermented wines in the world, and very popular in China. GABA is catalysed from glutamic acid by glutamic acid decarboxylase and exists widely in nature; its effects include calming nerves, resisting anxiety and detoxification etc. (Feudis De 1983; Haugstad et al. 1997; Lieve et al. 2011; Sergio et al. 1995; Thomas et al. 1984). It's an important inhibitory neurotransmitter (Niranjala et al. 1995) in the central nervous system of mammals, crustaceans and insects.

In recent years, it has been reported that an amino acid analyser, GC or LC-MS, column chromatography fluorescence assay and high performance liquid chromato- graphy (HPLC) have all been applied to the detection of γ-aminobutyric acid (Constantinos et al. 2004; Zhang and Alan 1997; Zhang and Sun 2005; Mao et al. 2011; Osborne et al. 1999; Silva et al. 2009; Ryutaro et al. 2012); however, the detection of GABA using the near infrared spectroscopy (NIR) method, employing chemometrics, has not previously been published.

The PLS method is widely used in many fields, such as chemistry, economics, medicine, psychology and pharmacy, to establish models. In particular, it has the advantage of setting a random variable if needed. For chemometrics, the PLS method has become a standard established tool of the multivariant model.

The near infrared spectrum includes valuable information such as bond strength, chemical composition, electronegativity and hydrogen bonds; for a solid sample, in addition to the above-mentioned parameters, it also includes information on scattering, diffuse-reflectance, polarization by reflection, sample particle and size etc. The routine methods of spectral analysis cannot be employed to extract the complicated and

Table 1 The content of γ-aminobutyric acid in rice wine

Sample No.	GABA (mg/L)	Sample No.	GABA (mg/L)
1	273.3320	16	277.8917
2	186.7935	17	317.5885
3	246.0835	18	260.3254
4	185.2436	19	210.2488
5	181.9210	20	179.5326
6	168.7020	21	157.6710
7	175.5635	22	265.4957
8	190.9920	23	163.5925
9	203.3363	24	222.2330
10	293.9145	25	215.6950
11	181.0190	26	217.9965
12	199.5757	27	269.0320
13	243.3935	28	273.7770
14	266.1015	29	191.8780
15	225.9898	30	250.6909

weak information from the near infrared spectrum; therefore, chemometrics has been introduced to near infrared spectrum analysis to effectively extract the information (Ryutaro et al. 2012).

In this paper, data from the near infrared spectrum of rice wine was analysed using a PLS method (Phil 1987) and quantified to give the γ-aminobutyric acid content in rice wine. It provides better results in terms of precision, stability and efficiency.

Materials and methods

Materials and apparatus

The test samples were classified into two groups, consisting of calibration and prediction. HPLC was employed to detect the content of GABA in rice wine for calibration; Table 1 shows the results of the HPLC determination.

Acquisition of the near infrared spectrum

The spectrum of rice wine was acquired using MPA near infrared spectroscopy with an optical fibre probe at 25 °C. With a detection waveband between 12500–4000 cm^{-1}, a scanning duration of 16 scans (an automatic collection during each scan of 16 points) and an instrument resolution of 8 cm^{-1}, the sample of rice wine was analysed using an optical fibre probe. Spectra were collected in triplicate for every sample and the average value of the spectra was obtained. Background scanning was applied to each sample to enable background correction; a sample spectrum is shown in Fig. 1.

Data processing and analysis

Data processing and analysis were executed using the PLS software of the quantitative analysis MATLAB software. The software operation interface is shown in Fig. 2

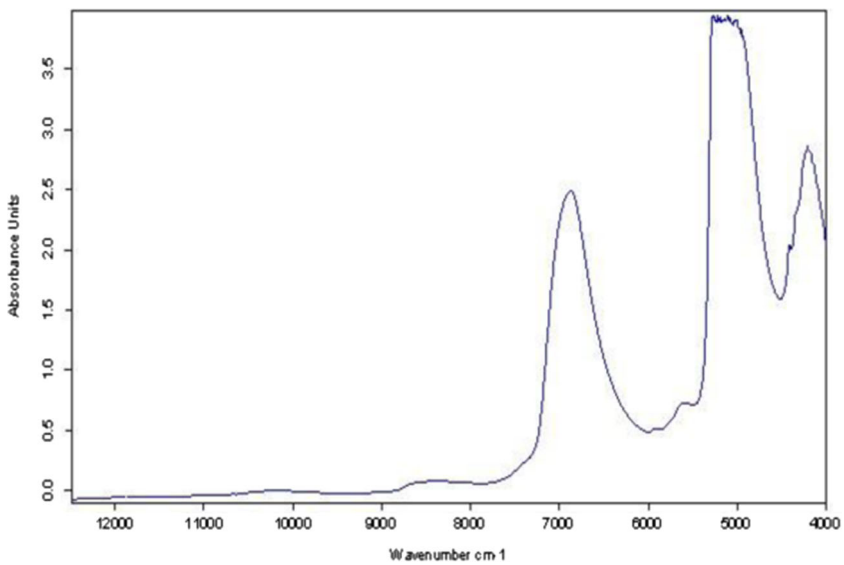

Fig. 1 Near infrared spectrum of rice wine

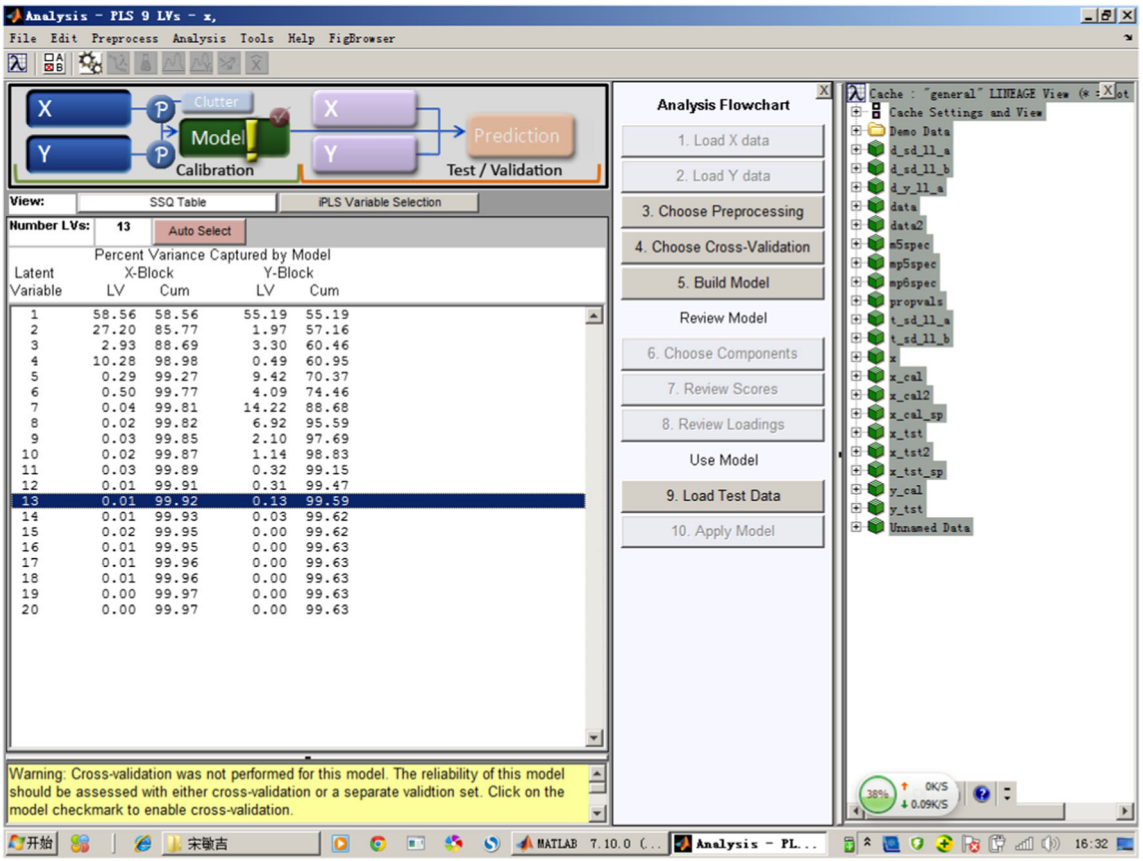

Fig. 2 The operational interface for MATLAB

Table 2 The value of prediction and set Unit: mg/L

PLS prediction	HPLC detector	PLS prediction	HPLC detector
273.3223205	273.3320	226.0029244	225.9898
186.817801	186.7935	277.8939183	277.8917
246.073031	246.0835	317.581345	317.5885
185.2646826	185.2436	260.3029468	260.3254
175.2979692	181.9210	210.2577379	210.2488
175.2979692	168.7020	179.4969437	179.5326
183.2682281	175.5635	157.6696101	157.6710
183.2682281	190.9920	265.5123383	265.4957
203.3364245	203.3363	163.634374	163.5925
293.9188751	293.9145	222.2462783	222.2330
180.9945620	181.0190	215.6724597	215.6950
199.5881844	199.5757	218.0171332	217.9965
243.3960585	243.3935	268.9875852	269.0320
266.1000037	266.1015	273.8337104	273.7770

Table 3 The stability experiment results of GABA detection in rice wine

Sample	Parallel Sample 1	Parallel Sample 2	Parallel Sample 3	Parallel Sample 4	Parallel Sample 5	Parallel Sample 6	RSD
1	306.2406	312.0598	308.1362	308.8122	310.2404	312.1105	0.7480 %
2	175.2980	177.2660	175.2981	180.2981	168.7020	176.2991	2.1778 %
3	243.3961	243.3935	243.4451	248.3163	246.5567	244.7845	0.8373 %
Average RSD							1.2544 %

Results and discussion

Experimental results

30 samples were used for calibration and experimental prediction. Firstly, the above acquired spectral data were treated using centralized normalization. Then, the data were quantitatively analysed using the PLS software of MATLAB. The optimal factor of 17 was determined through cross-validation. The samples were predicted from the calibration set; the prediction value and set is shown in Table 2.

In order to detect GABA in rice wine, a multivariant calibration PLS was used to establish a precise calibration model. The predicted content of GABA in rice wine is between 157.6696–317.5813 mg/L with a relative standard deviation of 0.01–5 %, proving that the result is accurate.

The stability of near infrared spectrum detection

Three groups of rice wine samples were simultaneously tested six times using the above-established detection method. The results are shown in Table 3.

The relative standard deviation of the three groups of simultaneously tested samples is 1.2544 %, which proves that the method is stable.

The testing results are satisfactory for the market sample; as seen in Table 4.

The rice wines on the market were tested using the near infrared method and after the results were verified by HPLC, the agreement was demonstrated. The relative standard deviation of the results is less than 5 % and the average relative deviation is 2.8774 %, thus, this NIR method is suitable for the detection of GABA content in rice wine.

Table 4 The testing results of the market sample

Sample	PLS prediction	HPLC detector	RSD
1	274.1229	265.4957	1.6247 %
2	149.1743	163.5925	4.4067 %
3	222.2330	208.3496	3.3317 %
4	234.9821	215.6950	4.4709 %
5	189.7552	191.8780	0.5532 %
Average RSD			2.8774 %

Conclusion

An optical fibre near infrared spectroscopy probe is an easy and rapid method for detecting the γ-aminobutyric acid content in rice wine; in addition, it takes less than 20 s to detect per sample. It is more precise as the related standard deviation for sample prediction is less than 5 %. It is more stable as the average relative standard deviation for a single detection is less than 1.5 %. The samples on the market were tested and the average relative standard deviation is 2.8774 %. We used the multivariant calibration PLS calibration method which is an established mature and reliable popular method, and is easy to apply and use.

Acknowledgments This work was supported by the General Administration of Quality Supervision Inspection and Quarantine of P.R. China (Grant No.2012.5) and Zhejiang Bureau of Quality and Technical Supervision (Grant No.20110236). We are delighted to acknowledge the assistance of Dr Liz and Mr Yuan Liu in revising the English, and the discussions with colleagues in our research group.

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