


Monitoring of total acidity content in continuous vinegar fermentation using a self-made modification of a micro-electro-mechanical system near-infrared spectrometer

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Abstract

This study evaluated the potential of a micro-electro-mechanical system (MEMS) near-infrared spectrometer for the on-line monitoring of total acids in the continuous fermentation process of rice vinegar and white vinegar. A self-made modification of the digital light processing NIRscan nano spectrometer was used for this purpose. As best pretreatment method, the multiplicative scatter correction was used to pretreat the raw spectra, which were subsequently subjected to a partial least square regression calibration. The results showed that total acids could be determined by this experimental setup with root-mean-square errors of predictions of 0.12% (w/v) and 0.27% (w/v) for rice vinegar and white vinegar, respectively. In conclusion, this low-cost MEMS near-infrared instrument can be applied to monitor total acids in the industrial continuous fermentation process of rice and white vinegar.

Keywords

White vinegar, rice vinegar, total acids, continuous fermentation, low-cost near-infrared spectrometer

Introduction

Vinegar is an acidic product of special importance for the enrichment of our diet, resulting from the desired or controlled oxidation of ethanol-containing substrates, and it is an important ingredient in vinegar drinks, such as apple vinegar beverage.

Vinegar production can be operated in three main processes: static, solid-state, and submerged “fermentation”. The latter is the quickest process and is suitable for industrial vinegar production because the fermentation parameters (temperature, oxygen, alcohol content, and acidity) can be strictly controlled.¹ In the modern vinegar industry, vinegar is mainly produced by continuous fermentation, and in order to control the quality of vinegar, it is important to monitor the fermentation process. As a quality indicator in vinegar, total acids (TA), including acetic acid, lactic acid, and other acids, is one of the most critical functional ingredients and influences the grade assessment of vinegar.² It also regulates blood glucose concentration, decreases blood pressure, and inhibits body fat accumulation.^{3,4}

Fermentation monitoring is an essential operation for vinegar production quality.⁵ Specifically, monitoring the change of TA is very important for the quality management of the process of vinegar fermentation. Till date, there is a bioprocess monitoring technique

in the food industry; however, this conventional analytical titration method is time-consuming, environmentally unfriendly, and laborious. Furthermore, it is inconvenient for analyzing large batch samples in fermentation.⁶ Undoubtedly, near-infrared (NIR) spectroscopy is the best choice for bioprocess monitoring since it has the advantages of not only being rapid and non-invasive but also it provides accurate real-time results of multi-parameters using multivariate methods.^{7,8} In recent years, NIR spectroscopy has been employed in the determination of fermentation products, such as cell cultures, dairy products, wines, and vinegar.⁹⁻¹¹ For vinegar, the NIR technique was applied for monitoring rice vinegar production by using Fourier-transform NIR or UV-VIS-NIR spectrometers, and onion vinegar by using a NIRSystems 5000 spectrophotometer.^{7,10,11} These previous works

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on vinegar bioprocess monitoring mainly focused on determining substrate parameters such as alcohol content, total sugars, and pH, as well as acetic acid content in the final product. However, the present study aimed to determine TA during continuous fermentation of white vinegar and rice vinegar, respectively, using a self-made modification of a micro-electro-mechanical system (MEMS) NIR spectrometer.

The progress in miniaturization of NIR spectrometers – which has taken advantage of new micro-technologies such as MEMS, micro-opto-electro-mechanical systems, and micro-mirror arrays or linear variable filters – has led to a drastic reduction of spectrometer size while allowing good performance due to the high-precision implementation of important elements in the final device.¹² Also, high-volume manufacturability further reduces costs and thereby contributes towards broader dissemination of such instruments for industrial monitoring and everyday-life applications.¹³

Based on the type of detector, the NIR spectrometers can be classified into two categories: array-detector and single-detector instruments. Compared to an array detector, the price for a single detector is much lower, and in an attempt to further reduce the hardware costs, new developments focus on systems with single detectors. The digital light processing (DLP) NIRscan Nano EVM (Dallas, TX, USA) is based on Texas Instruments' digital micro-mirror device (DMD™) in combination with a grating and a single-element detector and covers the wavelength range from 900 to 1700 nm. Documentation of on-site applications can be found in recent reports.^{14–16} For the present work, the original DLP NIRscan Nano EVM has been modified by dismantling the two light sources and combining a new light source (see below) with an optical light fiber in a 3D-printed adapter (Figure 1). This hardware modification can be used for monitoring liquid samples and has been used for the determination of the content of TA and total polyphenols in the fermentation broth of Mulberry Vinegar in a laboratory setting.¹⁷ In the present feasibility study, the experimental set-up was used to investigate the on-line detection of TA in the industrial fermentation process of white and rice vinegar.

Materials and methods

Vinegar samples

Two kinds of samples, rice vinegar and white vinegar, were measured in this study. They were collected from continuous fermentation tanks (Jiangsu Hengshun Vinegar Co. Ltd) at different fermentation time intervals. For the present investigations, a total of 50 rice vinegar and 50 white vinegar samples were collected.

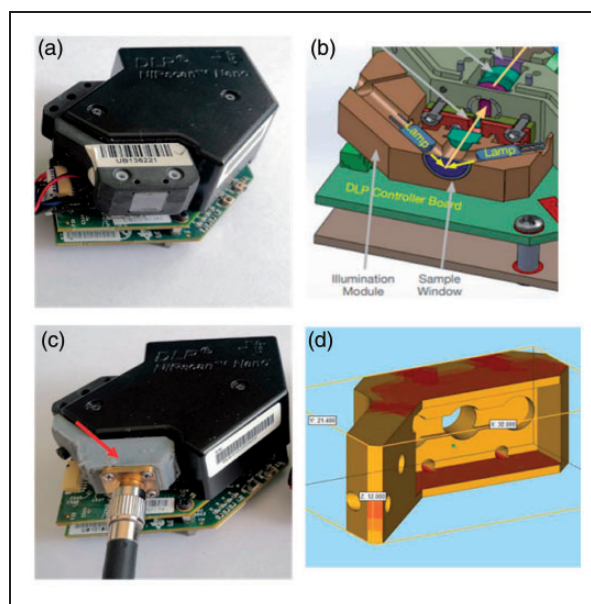


Figure 1. Schematic of original spectrometer and self-made modification. (a) and (b) Original DLP NIRscan Nano EVM, (c) modification of the DLP NIRscan Nano EVM by the adapter for combining a new light source with an optical fiber, (d) technical schematic of the 3D-printed adapter. DLP: digital light processing.

Spectra measurement

The spectral measurement system was equipped with an HL-2000 light source (Ocean Optics, Inc., Orlando, FL, USA) and coupled to an optical fiber. The liquid samples were measured in a 1 mm path length transmission cuvette at 30°C, and a reference spectrum was recorded with an empty cuvette before the spectra acquisition. The spectrum of each sample was the average of 32 successive scans with a total scan time of 8.32 s and a spectral range of 917–1643 nm. Each sample was measured three times, and the average of three spectra was further processed as the final spectrum.

Reference determination

TA was determined by acid–base titration with 0.1 mol NaOH using phenolphthalein as an indicator, according to the National Standard of the People's Republic of China, 2006.

Spectral data analysis

The white and rice vinegar samples were separated into individual calibration and test sets with a ratio of 2:1, respectively, by a hierarchical selection procedure.^{18,19} The number of calibration set and test set samples are summarized in Table 1.

Spectral pretreatment. To improve the spectral model's predictive capability, unwanted sources of variability due to noise, light scatter, and environmental disturbance should be eliminated.²⁰ In this work, the

standard normal variate (SNV), first order (1st) derivative, second order (2nd) derivative, multiplicative scatter correction (MSC) were applied. For the 1st and 2nd derivative, the Savitzky-Golay smoothing procedure of five data points and a 2nd order polynomial was used.

Partial least square calibration. Calibrations were performed using the linear partial least square (PLS) method to determine the TA content. Since the number of factors has a significant influence on calibration performance, the optimal numbers of factors were selected using a 20 fold internal cross-validation. In detecting outliers, Hotelling statistics (or T^2) was used to define statistical boundaries. For rice vinegar, two samples were deleted as outliers from the calibration set. External test sets were applied to evaluate the performance of the calibrated models.

Evaluation of calibration performance. The calibration statistics parameters were employed to assess the performance of the models developed by the PLS regression method. The coefficient of determination R^2 was a measure of the linearity, the root-mean-square errors of cross-validation (RMSECV) and prediction (RMSEP) were indicators for the accuracy of the established model.²¹ The residual predictive deviation for cross-validation (RPD_{cv}) was calculated as the ratio of the standard deviation (SD) of the reference data to RMSECV. High RPD_{cv} values indicate a good prediction model; an RPD value greater than three can be considered as very good for prediction

purposes.^{22,23} The smaller the RMSE values and the closer they were to each other, the higher the prediction accuracy and robustness of the calibration model. The closer R^2 was to one, the better the agreement between the predicted and the reference values.²⁴

Results and discussion

Raw NIR spectra

The raw NIR calibration spectra of the two vinegar species are shown in Figure 2. The spectra have an absorption band around 1159 nm, which can be assigned to 2nd overtones of CH/CH₂/CH₃ functionalities. The absorption peaks at 1440 nm and 967 nm are related to the 1st overtone of the $\nu(\text{OH})$ and 2nd overtone of the $\nu(\text{NH})$ stretching vibrations, respectively.²⁵

Reference values

The descriptive statistics of the TA content in the investigated vinegar samples are summarized in Table 1. For the calibration sets, the ranges of TA in rice and white vinegar were 7.93–9.74% (g/100 mL) and 7.22–11.24% (g/100 mL), respectively, and the corresponding values of mean \pm SD were $8.70 \pm 0.53\%$ (g/100 mL) and $9.37 \pm 1.12\%$ (g/100 mL), respectively. The similarity of values for the test and calibration sets demonstrates that the samples were reasonably separated.

Table 1. Statistical results of TA (g/100 mL) content of rice and white vinegar.

Sample	Data set	Number	Mean	Max	Min	Range	Std.
Rice vinegar	Calibration set	33	8.70	9.74	7.93	1.81	0.53
	Test set	17	8.74	9.74	7.94	1.80	0.57
White vinegar	Calibration set	33	9.37	11.24	7.22	4.02	1.12
	Test set	17	9.35	11.12	7.3	3.82	1.18

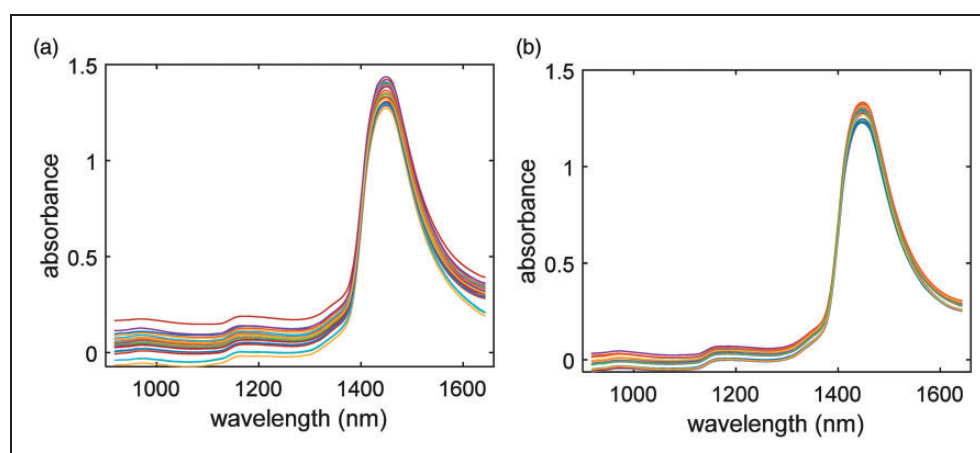


Figure 2. The raw NIR spectra of vinegar; (a) rice vinegar, (b) white vinegar.

Spectral pretreatment

For both kinds of vinegar, different pretreatment methods, SNV, MSC, 1st derivative, and 2nd derivative, were applied. The pretreated spectra are shown in

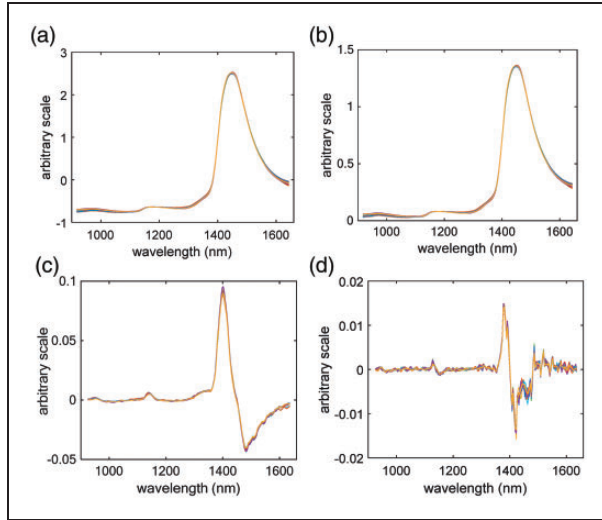


Figure 3. The rice vinegar spectra after pretreatment by (a) SNV, (b) MSC, (c) 1st derivative, and (d) 2nd derivative.

Figure 3, in which all baseline shifts were corrected. While the SNV and MSC procedures correct light scattering effects, the 1st and 2nd derivative spectra highlight absorption band positions and superpositions.

Analysis of the calibration data

In PLS calibrations, the number of factors has a significant effect on the calibration performance. Fewer factors could result in building an inadequate model, while too many factors could cause overfitting. In this work, the optimal number of factors was determined by internal cross-validation. The results of the calibration statistics analysis are summarized in Table 2.

For different pretreatment methods, the capability to extract spectral information was different. In this study, MSC turned out to be the best pretreatment procedure. For rice vinegar, the RMSEC and RMSECV were 0.13 g/100 mL and 0.16 g/100 mL, and their corresponding R^2_C and R^2_{CV} values of 0.9426 and 0.9249, respectively, demonstrated a high calibration performance. The RPD_{CV} value of 3.31 clearly proved that the developed calibration models can accurately predict the TA content of the investigated vinegar samples. The test set, which represented unknown

Table 2. The calibration results for the NIR spectra of rice and white vinegar.

Samples	Pretreatment methods	LVs	RMSEC (g/100 mL)	RMSECV (g/100 mL)	RMSEP (g/100 mL)	R^2_C	R^2_{CV}	R^2_P	RPD_{CV}
Rice vinegar	None	6	0.12	0.18	0.14	0.9447	0.8778	0.9382	2.94
	1st Der	4	0.13	0.20	0.17	0.90	0.8726	0.9161	2.65
	2nd Der	4	0.14	0.21	0.17	0.9300	0.8290	0.9161	2.52
	SNV	5	0.10	0.16	0.15	0.9621	0.9216	0.9287	3.31
	MSC	5	0.13	0.16	0.12	0.9426	0.9249	0.9588	3.31
White vinegar	None	5	0.24	0.33	0.22	0.9504	0.9035	0.9612	3.39
	1st Der	4	0.28	0.38	0.37	0.9344	0.8772	0.8915	2.95
	2nd Der	3	0.25	0.35	0.31	0.9488	0.9181	0.9242	3.20
	SNV	4	0.21	0.27	0.27	0.9648	0.9460	0.9442	4.15
	MSC	5	0.21	0.27	0.27	0.9638	0.9473	0.9482	4.15

LV: latent variable; RMSEC: root-mean-square errors of calibration; RMSECV: root-mean-square errors of cross-validation; RMSEP: root-mean-square errors of prediction; SNV: standard normal variate; MSC: multiplicative scatter correction.

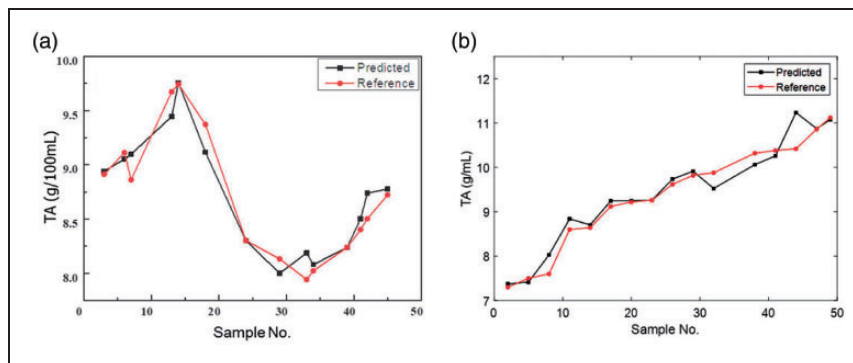


Figure 4. Predicted and reference TA values of the test set samples withdrawn during continuous fermentation, (a) white vinegar (b) rice vinegar.

samples, was used to validate the prediction capability of the developed calibrations. The achieved results confirmed that the calibrations were robust and the predicted TA contents were accurate (Figure 4). For white vinegar, similar, high calibration performance was achieved after SNV and MSC pretreatment (Table 2). Especially the RPD_{CV} values of 4.15, which were higher than those for rice vinegar, demonstrate a high prediction capability.

In Figure 4, the good agreement of predicted and reference TA values of white and rice vinegar as a function of changing TA values demonstrated that the vinegar fermentation process can be reliably monitored.

Conclusions

The results achieved in the present feasibility study have clearly demonstrated, that the self-made modification of the low-cost MEMS NIR spectrometer can be used for the fast and accurate on-line determination of TA in the fermentation process of white and rice vinegar. It is of note, that this instrumental setup can also be used for other applications of concentration monitoring in liquid process samples.

Declaration of conflicting interests

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