Asian Journal of Chemistry; Vol. 24, No. 2 (2012), 822-826

ASIAN JOURNAL OF CHEMISTRY

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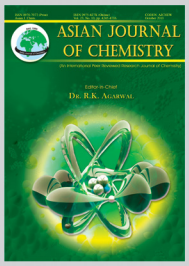

Identification of the Types of Parched Areca Seed by Near Infrared Spectroscopy

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(*Received*: 6 April 2011; *Accepted*: 19 October 2011) AJC-10538

This research was aimed to establish a rapid and automated analytical method for the identification of different types of parched areca seed (AS) (raw areca seed, parched-yellow areca seed, seorched areca seed and charring areca seed) by near infrared spectroscopy (NIR). Twenty kinds of areca seed were selected from 60 kinds obtained from various places and then were parched by an online-type and non-contact temperature measurement system invented by our study team; based on the colour, parching temperature and time, concentration of main effective constituent and the results of cluster analysis of 290 samples. The near infrared identification model which could identify four types of parched areca seed fast and accurately was establish after pretreated with vector normalization and first derivative method. The proposed method is accurate and robust which could be used for the identification of other traditional Chinese medicine.

Key Words: Near infrared spectroscopy, Areca seed, Parching type, Identification.

INTRODUCTION

Based on the theory of traditional Chinese medicine (TCM), the majority herb should be processed before clinical applications and the drug efficacy would be changed in different processing methods, for example areca seed (AS), the dry mature seed of *Areca catechu* L. The processed types mainly include raw areca seed, parched-yellow areca seed, seorched areca seed and charring areca seed according to the degree of the parching. Raw areca seed is mainly used as anthelmintic with strong side effect; parched-yellow areca seed, anthelmintic with weaker side effect; seorched areca seed, digestant and charring areca seed, antistatic[1-3]. So herb of different processed types should be strictly identified in clinical application.

The traditional method for identifying processing type principally based on colour, smell and processing method, which needs certain individual experience and specialized knowledge. However, these characters often changes when the habitat and processing method are different. It is difficult to identify processing type automatically and fast by the traditional method.

Recently, near infrared spectroscopy opens many interesting perspectives in pharmaceutical analysis, both qualitatively and quantitatively[4-9]. Near infrared, due to its rapid analysis, requirement of simple or no sample preparation, accuracy for multi-parameters and excellent precision, is routinely preferred and increasingly becoming one of the most efficient analytical tools for rapid and automated identifying different processing type[10-12].

An online-type and non-contact temperature measurement system (ONTMS) was invented by our study team and had been patented (PR China Patent No.: ZL200520200614.0). In the parching process of areca seed, it could display and control the temperature of the herbal medicine roaster.

In the present investigation, near infrared was applied to establish a rapid and automated identification model of different types of parched areca seed based on the colour, parching temperature and time, concentration of main effective constituent and results of cluster analysis of 290 samples. Furthermore, a novel technology, an online-type and non-contact temperature measurement system (ONTMS), was used to display and control the temperature of the herbal medicine roaster in the parching process of areca seed.

EXPERIMENTAL

Sixty different kinds of areca seed were collected from various drug stores or traditional Chinese medicine markets:

24 kinds were collected from Yunan Province in P.R. China (No.: YN001-YN024); 21 kinds, Guangxi Province in P.R. China (No.: GX025-GX045); 6 kinds imported (Burma: 3 kinds; Indonesia: 1 kind; Vietnam: 1 kind) (No.: J046-J051); 9 kinds unknown (No.: WZ052-WZ060)}. Twenty kinds of areca seed were selected carefully from these 60 kinds and then parched by online type and non-contact temperature measurement system. Parched areca seed samples were collected at 0, 2, 4, 8, 10, 11, 12, 13, 14 and 15 min (16 or 17 min for some of the kinds) before reaching 210 ºC. For example, there were 1 parched samples of GX036 which were numbered from GX036-0 to GX036-12. The temperature and time was recorded by online type and non-contact temperature measurement system while the parched samples were collected. Fig. 1(a) shows the parched samples of one kind of areca seed.

Detection method: The near infrared spectra of areca seed were recorded using a Bruker Matrix-I FT-NIR spectrometer (Bruker Optik, Ettlingen, Germany) equipped with a PbS detector, sample cup and rotary tables. The system was operated by OPUS spectral acquisition and processing software (Bruker Optik, Ettlingen, Germany). The spectra were obtained at a resolution of 8 cm^{-1} over a wavelength range of 12500-3600 cm^{-1} with 64 scans per spectrum and air absorbance was recorded as the reference standard. Fig. 1(b) was the near infrared spectra of the parched samples in Fig. 1(a).

The concentration of alkaloid was detected using Agilent 1100 HPLC system (Agilent Technologies Inc., USA) consisting of UV-VIS detector at a wavelength of 212 nm over a Nucleosil 100-5 SA column (250 mm × 4.6 mm, 5 µm). The elution system was composed of methanol-water-phosphoric acid (60:40:0.3, pH = 3.8, adjusted by 25 % of ammonia). Chromatographic peaks were identified by comparing their retention time against the standard references.

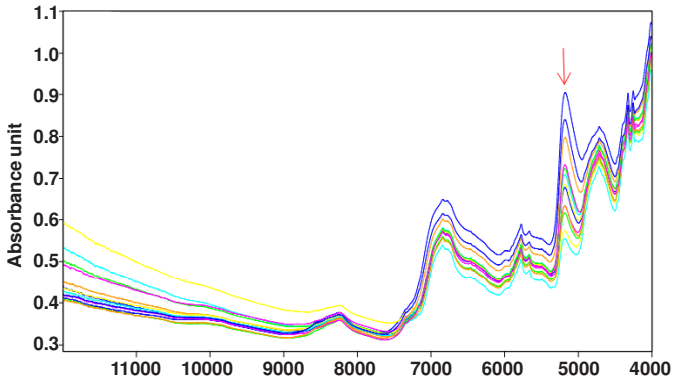


Fig. 1. (b) Raw NIR spectra of parched samples (along the arrow direction, the spectra are the sample a-l in Fig. 1(a) in turn

RESULTS AND DISCUSSION

Classification of areca seed samples: Due to the different habitat of areca seed and processing method of some place, it was difficult to classify and identify processing type accurately and fast through the colour and parched temperature by the traditional method. As shown in Fig. 2, raw areca seed YN006 and YN013 from the same habitat Yunnan province have different colours and thickness sheets (YN013: about 0.31 cm; YN006: about 0.18cm) and raw areca seed GX036 produced from Guangxi province has darker colour and thinner sheets, so they had different parched extent and colours in the same temperature when parched. areca seed shown in Fig. 5, 3 kinds of alkaloid content (arecoline, arecaidine and guvacine) in 60 kinds of raw areca seed were different due to the above reason.

The cluster analysis divides similar spectra into groups. First, the OPUS software calculates the spectral distances between all spectra that indicate the degree of spectral similarity.

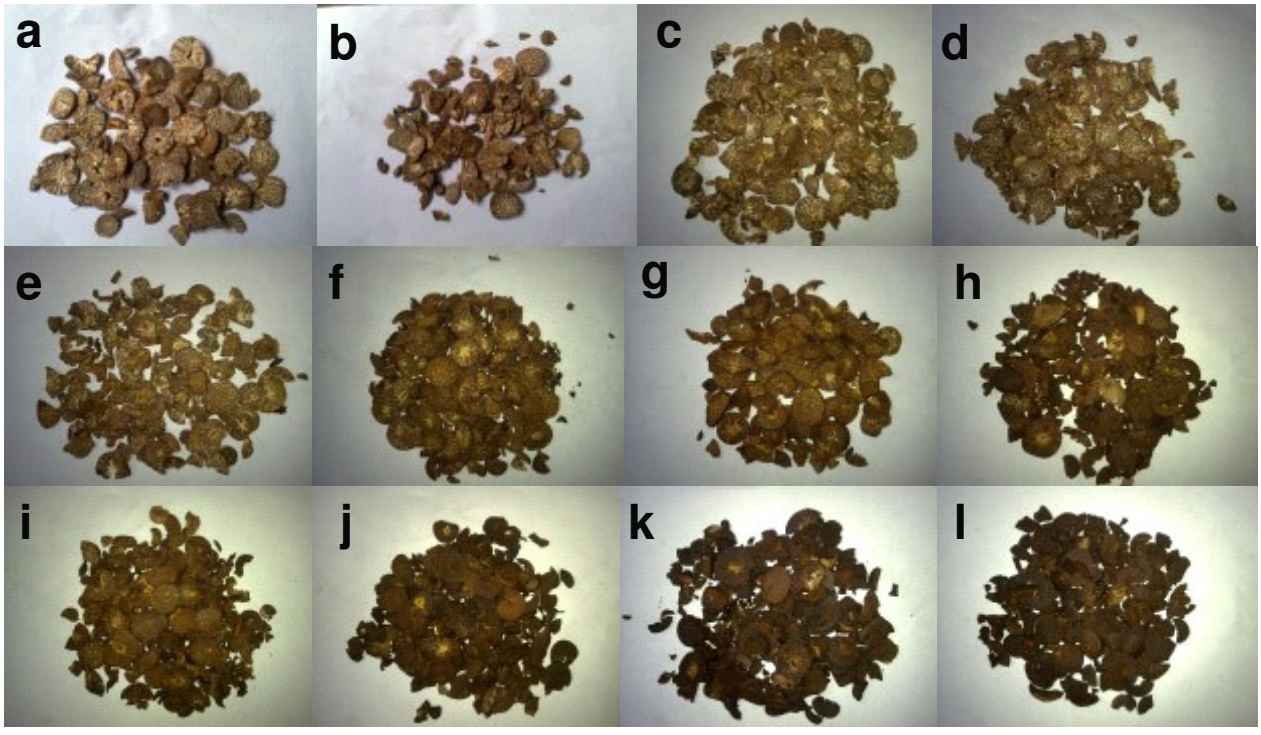


Fig. 1. (a) Frying samples collected at 0 min (a), 2 min (b), 4 min (c), 6 min (d), 8 min (e), 10 min (f), 11 min (g), 12 min (h), 13 min (i), 14 min (j), 15 min (k) and 16 min (l), respectively

Fig. 2. Raw areca seed samples

The higher the distance between two spectra, the higher the spectral distance will be. Then the two spectra (spectrum/spectrum or spectrum/cluster) with the smallest distance are merged again into a new cluster. This procedure will be repeated until only one big cluster will be left. In order to offer information on the classification of areca seed, The cluster analysis of 20 kinds of areca seed were carried out. Fig. 3 shows 3 simplified dendrograms of the parched samples of YN006, YN013 and GX036; the y-axis of the dendrograms shows the spectral distances between different clusters; the horizontal lines indicate the fusion levels, which are the spectra distances of the different clusters and spectra prior to new clustering.

As shown in Table-1, this study overall evaluated the colour, parching temperature and time, concentration of main effective constituent (arecoline, arecaidine and guvacine) and results of cluster analysis for the classification of areca seed

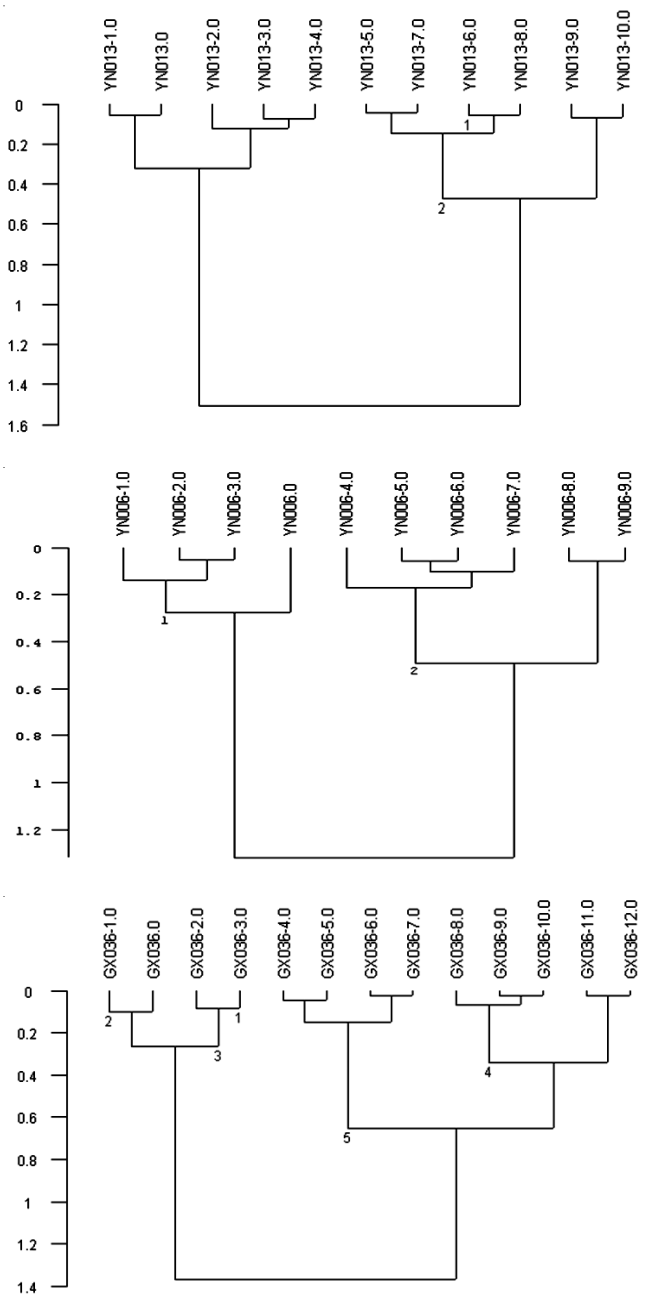


Fig. 3. Results of cluster analysis

samples, by which we got 60 samples of raw areca seed, 40 samples of Parched-yellow areca seed, 44 samples of Seorched areca seed, 41 samples of Charring areca seed and 105 samples of other type (the samples didn't belong to the above 4 types).

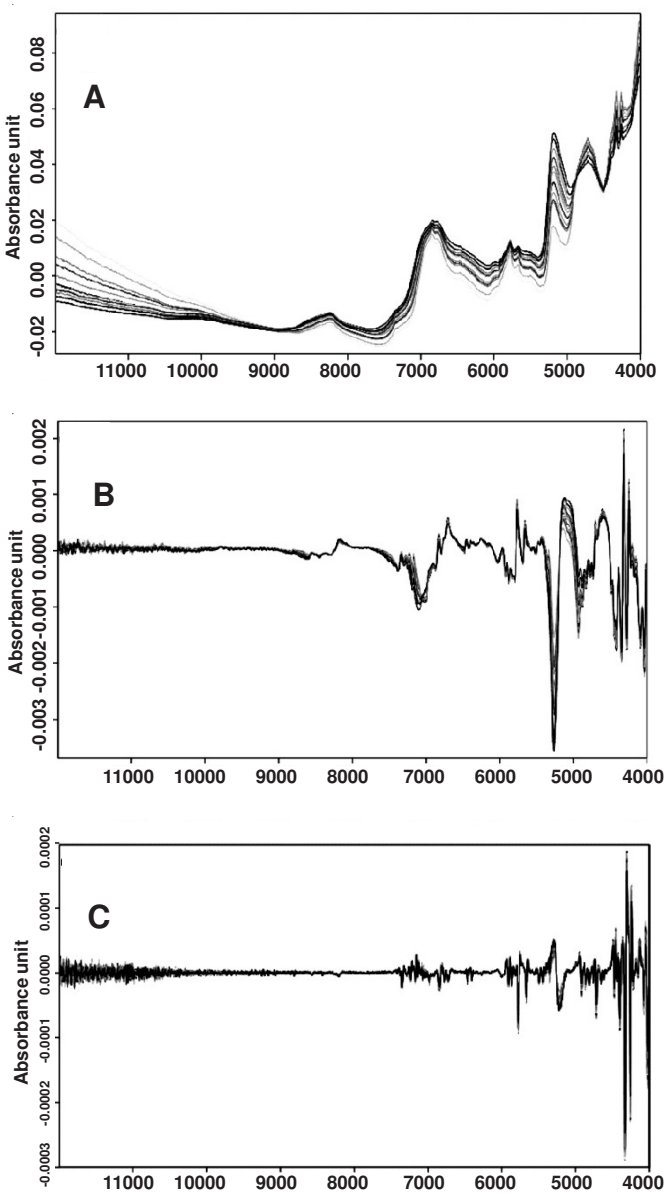
Data analysis: According to the above classification of areca seed samples, samples were selected randomly for validation

TABLE-1
INFORMATION OF DIFFERENT TYPES OF PARCHED ARECA SEED

	Raw AS	Parched-yellow AS	Seorched AS	Charring AS
Colour	Amber, marron	Yellow	Dark yellow	Dark brown
Temperature (ºC)	0	110-145	170-185	195-205
Parched time (min)	0	6-8	11-13	15-17
Arecoline (mg g^{-1})	4.872-10.60	4.739-8.090	5.240-8.041	2.832-6.274
Arecaidine (mg g^{-1})	0.4461-1.987	0.4870-1.473	0.6626-1.715	0.5808-1.959
Guvacine (mg g^{-1})	0.8040-5.109	0.9393-4.726	0.5025-3.830	0.0304-2.556
Number of samples	60	40	44	41

analysis, thus 100 samples were chosen for the validation set and the remaining 190 samples were for the calibration set.

Scrutinized from the spectra in Fig. 1(b) and Fig. 4, it reveals that some intensive spectral peaks are mainly in the region of 8500-4000 cm^{-1}. These intensive peaks are caused by the stretch or deformation vibration of -CH, -NH, -OH and -SH functional groups. Therefore, near infrared spectra in the region of 8500-4000 cm^{-1} contain much chemical information. Additionally, some spectral regions exhibiting a high noise level (*e.g.*, 10,000-9000 and 5000-4000 cm^{-1}) should be excluded from next data processing. The spectral region of 9000-5000 cm^{-1} was, therefore, selected for calibration PLS model.



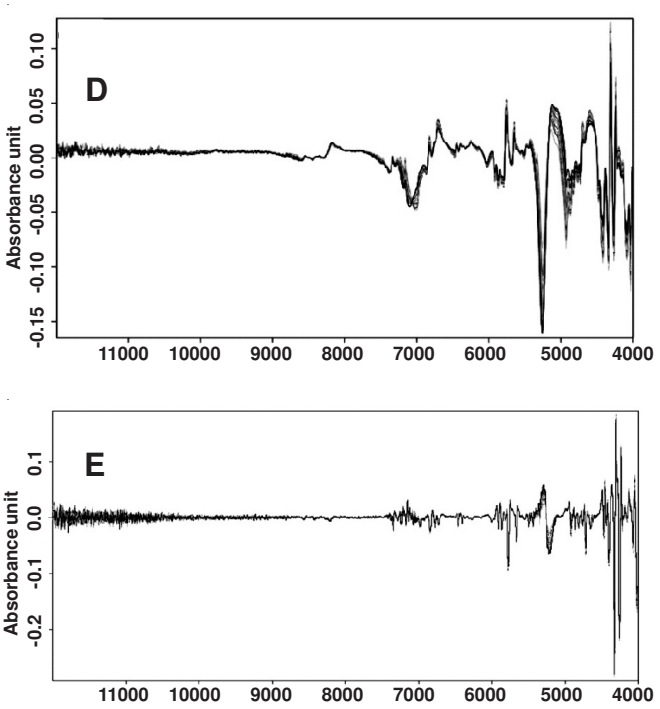


Fig. 4. Pretreated spectral of Fig. 1(b): (A) vector normalization (VN), (B) first derivative, (C) second derivative, (D) first derivative + vector normalization and (E) second derivative + vector normalization

The OPUS software provides 5 important spectral pretreatment methods, including: vector normalization (VN), first derivative, second derivative, first derivative + vector normalization and second derivative + vector normalization. Fig. 4 shows the spectral pretreated by the above methods.

In the spectral pretreatment process, the PLS model is validated by leave-one-out-cross-validation, so the same samples are used both for model estimation and testing. A few samples are left out from the calibration set and the model is made on the remaining samples. The type for the left-out samples is predicted and the prediction results are computed. This process is then performed with another subset of the calibration set and repeated until every object has been left out once; then all prediction results are combined to select possible methods for the near infrared identification model.

Then 5 good models were got from these possible methods and used to predict the type of 100 samples in the validation set. As shown in Table-2, Model. 5 had the best predicting accurate, so it was the optimized model for the near infrared identification model.

Regional diversity of the areca seed samples: It has been reported that the drug efficacy of areca seed is affected by cultural characteristics, climate and soil conditions. As such, these factors may cause variation of the drug efficacy. Because

TABLE-2
PREDICTED RESULT OF FIVE METHODS FOR THE IDENTIFICATION MODEL

	Spectral pretreatment method	NIR wavelength range (cm^{-1})	Predicting accurate (%)
Model 1	Vector normalization	7502.1-4246.7	87
Model 2	Vector normalization	7502.1-6098.1, 5450.1-4246.7	89
Model 3	First Derivative	7502.1-6098.1, 5450.1-4246.7	79
Model 4	First Derivative + vector normalization	7502.1-4246.7	92
Model 5	First Derivative + vector normalization	7502.1-6098.1 5450.1-4246.7	96

the areca seed samples were collected from different places as shown in Fig. 5, so this near infrared model had good representation and durability.

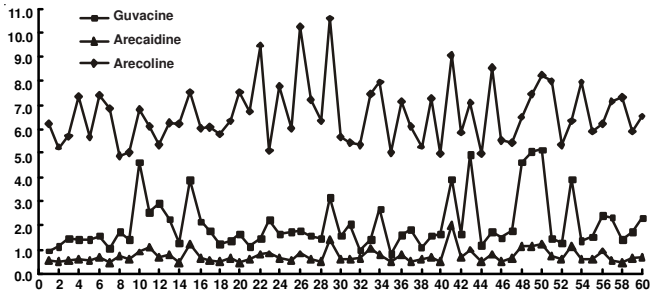


Fig. 5. relationship between the areca seed samples' places of produce and the content of alkaloid (No. 1-24 from Yunan Province in P.R. China; No. 25-45 were from Guangxi Province in P.R. China; No. 46-51 imported (No. 47-49: Burma; No. 50: Indonesia; No. 51: Vietnam) No. 52-60: unknown)

Conclusion

In this study, near infrared provided accurate and rapid identification of different types of parched areca seed) (raw areca seed, parched-yellow areca seed, seorched areca seed and charring areca seed), which overcame the limitation of the traditional method; overall, this method shows great promise in rapid online analysis and quality control of industrial manufacturing processes.

ACKNOWLEDGEMENTS

The authors graciously acknowledged the financial support provided by the National Sciences Foundation of P.R. China (No. 30973942). The authors also thank Bruker Optik Ltd., who provided the instruments and analysis instruction and the Sichuan Traditional Chinese Medicine Material Limited Company, who aided with areca seed sample parching.

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