Food Control 78 (2017) 144–149

Contents lists available at ScienceDirect

Food Control

journal homepage: www.elsevier.com/locate/foodcont

Gum Arabic authentication and mixture quantification by near infrared spectroscopy

Yongjiang Dong [a, 1], Klavs Martin Sørensen [b, *, 1], Sailing He [a], Søren Balling Engelsen [b]

[a] Centre for Optical and Electromagnetic Research, Zhejiang Provincial Key Laboratory for Sensing Technologies, State Key Laboratory Modern Optical Instrumentation, JORCEP, Zhejiang University, Hangzhou 310058, PR China
[b] Spectroscopy & Chemometrics, Department of Food Science, University of Copenhagen, Rolighedsvej 26, 1958 Frederiksberg, Denmark

ARTICLE INFO

Article history:
Received 15 September 2016
Received in revised form
18 January 2017
Accepted 1 February 2017
Available online 3 February 2017

Keywords:
Gum Arabic
Near infrared (NIR) spectroscopy
Sampling of 'tears'
Acacia senegal
Acacia seyal
Principal component analysis (PCA)
Partial least squares (PLS) regression

ABSTRACT

A rapid and reliable method is developed for Gum Arabic authentication based on Near Infrared (NIR) spectroscopy and chemometric methods. On a large industrial collection of authentic gum Arabics, the two major Acacia gum species, *Acacia senegal* and *Acacia seyal* could be assigned perfectly by the NIR spectroscopic method. In addition, a partial least squares (PLS) regression model is calibrated to predict the blending percentage of the two pure gum types, producing an accuracy, root mean square error of cross validation (RMSECV) of 2.8%. Sampling of the Gum Arabic 'tears' is discussed, and it was determined that subsamples from three 'tears' is required for a representative result. It is concluded that NIR spectroscopy is a very powerful and reliable method for authenticity testing of Gum Arabic species.

1. Introduction

Gum Arabic is one of the most ancient and popular natural gums and can be traced back to 2650 BCE (A. M. H. Abuarra, 2014). According to the definition of the Joint Expert Committee for Food Additives (JECFA), gum Arabic are dried exudate lumps, the so-called tears, obtained from the stem and branches of Acacia trees (Phillips, Ogasawara, & Ushida, 2008). There are more than 1000 species of the genus Acacia gums (A. Abuarra, Hashim, Bauk, Kandaiya, & Tousi, 2014), but only two of the Acacia species are significant for commercial purposes: *Acacia senegal* (L.), which is considered to be the best in quality due to a low quantity of tannins (Egadu, Mucunguzi, & Obua, 2007) and comprises the majority of global trade, and *Acacia seyal* (Del.), which produces a lower grade of gum (Ibrahim, Osman, & Hassan, 2013). Acacia trees are abundant in central Sudan, central and West Africa, tropical and semi-tropical areas of the world (Hadi, Elderbi, & Mohamed, 2010; Wyasu & Okereke, 2012). Sudan is the leading producer of Acacia gums worldwide, followed by Nigeria, Chad, Mali and Senegal (Vanloot, Dupuy, Guiliano, & Artaud, 2012). *A. Senegal* and *A. seyal* exudates exist as a multifunctional hydrocolloid with a highly branched, neutral or slightly acidic, arabino-galactan-protein complex containing calcium, magnesium, and potassium (Renard, Lavenant-Gourgeon, Ralet, & Sanchez, 2006). The molecular structure of the carbohydrate moieties of both gum Arabics are constituted of chains of 1,3-linked β-D-galactopyranosyl units with sidechains including primarily β-D-glucuronopyranose, α-L-arabinofuranose, α-L-rhamnopyranose, and 4-O-methyl-β-D-glucuronopyranose (Li, Gan, Liu, Lin, & Huang, 2014). Gum Arabic has wide applications, mainly in the food industry due to its emulsifying, stabilizing, thickening, and binding properties, which makes it useful for applications such as confectionery products (Verbeken, Dierckx, & Dewettinck, 2003), beverages (Buffo, Reineccius, & Oehlert, 2001; Mirhosseini, Tan, Hamid, & Yusof, 2008), fruits (Maqbool, Ali, Alderson, Zahid, & Siddiqui, 2011), and as a micro-encapsulating agent (Butstraen & Salaun, 2014). In addition, gum Arabic is also widely used for industrial purposes as in traditional lithography, printing, textiles (Patel & Goyal, 2015), and pharmaceutical applications (Ali, Ziada, & Blunden, 2009).

Authentication of food ingredients is an important issue for

* Corresponding author.
E-mail address: kms@food.ku.dk (K.M. Sørensen).
[1] Yongjiang Dong and Klavs Martin Sørensen has contributed equally to this work.

http://dx.doi.org/10.1016/j.foodcont.2017.02.002
0956-7135/

industrial quality control and international trading (Sørensen, Khakimov, & Engelsen, 2016), in particular in cases such as the two Acacia gum species which can be traded in a freeze-dried or powdered form. Conventional methods to characterize (Gashua, Williams, Yadav, & Baldwin, 2015) and to classify (Jurasek, Varga, & Phillips, 1995) the two types of gums were based on analyzing different physical and chemical parameters, such as intrinsic viscosity, total nitrogen, sugar composition, and total glucuronic acid. Using optical rotation is also an effective approach to classify *A. senegal* and *A. seyal* (Biswas & Phillips, 2003), however, this univariate method can relatively easily be "cheated" by adding sugars. Compared to these complex, time-consuming and less-sensitive techniques, spectroscopic techniques are more rapid, effective and easily implemented, inspiring their development for gum authentication applications. Nuclear Magnetic Resonance (NMR) is an effective analytical technology to identify *A. senegal* and *A. seyal* (Nie et al., 2013b, 2013a), but rather inaccessible for industrial high throughput screening purposes. Infrared (IR) spectroscopy and Raman spectroscopy, are also very useful as more convenient and common methods. In combination with chemometrics, IR was used to identify gum from other organic binding media such as waxes and resins (Sarmiento et al., 2011), and to classify different gums (Prado, Kim, Özen, & Mauer, 2005). Vanloot et al. has demonstrated the use of IR spectroscopy to classify *A. senegal* and *A. seyal* (Vanloot et al., 2012). Also, Raman spectroscopy has shown promising capability for identifying Arabic gum from other binder materials (Pallipurath, Skelton, Ricciardi, Bucklow, & Elliott, 2013) and for differentiating between gums of different origin (Srivastava, Wolfgang, & Rodriguez, 2016).

Near infrared (NIR) spectroscopy, which has the advantage of being robust, cost-effective and requiring less sample preparation, has a long record of being used widely for industrial food analysis applications (Luypaert, Massart, & Vander Heyden, 2007; Massie & Norris, 1975; van den Berg, Lyndgaard, Sørensen, & Engelsen, 2013; Williams & Norris, 1987) and should also be promising for gum characterization. Indeed, the near infrared technique has been used to study bean gum mixed with other biopolymers (Lundin, Stenlöf, & Hermansson, 1998), to determine the molecular weight of xanthan gum (Song et al., 2015), and to identify the gum Arabic as a paint binder (Ricciardi et al., 2012). Thus, the feasibility of using NIR spectroscopy for quality control of Acacia gum has been demonstrated, however, to our knowledge, no previous attempt has been made to discriminate between the two gum Arabic species using NIR spectroscopy. Quantification of gum mixtures is another interesting issue for gum characterization and authentication, as powdered gum Arabic may be easily adulterated by the addition of cheaper and more inferior gums. Prado et al. accomplished the quantitative analysis of individual "gum in gum" mixtures using IR spectroscopy and partial least squares regression (Prado et al., 2005). Vanloot et al. made a basic test on the adulteration of *A. senegal* and *A. seyal* using IR spectroscopy (Vanloot et al., 2012). Also, to our knowledge, the present study is the first to use NIR spectroscopy to study the two Acacia gums mixed with each other at different concentrations.

The primary aim of the present work is to investigate the effectiveness and reliability of the NIRS technique for the authentication of two Acacia gum exudates using a large industrial sample collection. Gum mixtures are used for calibration model building in order to predict the two Acacia gums.

2. Materials and methods

2.1. Gum sample preparation & measurements

A total of 26 Acacia gum samples were selected from a large industrial collection provided by Toms Group A/S (Ballerup, Denmark). The selected collection is composed of *A. senegal* samples ($n = 19$) and *A. seyal* samples ($n = 7$) originating from various provenances. Only samples with unambiguous identification were used in the following experiments.

Experiment 1 (see Fig. 1): for each of the 26 selected Gum Arabic samples ten subsamples were prepared by randomly selecting approximately 15 g of the non-uniform gum Arabic tears and then ground into a fine powder with a coffee grinder mill. This experimental design produced a total of 260 separate powder samples. All samples were processed, labelled and stored in airtight containers before any measurements.

Near-infrared spectra of the 260 samples were recorded in a random order. Measurements were conducted using a QFA Flex Fourier transform spectrometer (Q-Interline A/S, Roskilde, Denmark) equipped with a reflectance kinetic powder sampler that rotates a vial with the gum Arabic powder over the instrument window. Spectra were recorded in the range from 1100 nm to 2500 nm using an InGa detector with a 16 cm^{-1} resolution and 512 scans. The spectra were converted to log(1/R) units using a PFTE-filled vial as a background reference. The background reference was measured every hour of the experiment using the same measurement conditions.

Experiment 2: In this experiment three samples of each of the *A. senegal* and *A. seyal* types were chosen randomly (see Fig. 1). Pool samples were produced for each of these selections with an equal amount of the 10 available subsamples (from experiment 1). The pool samples were then paired, again randomly, producing three pairs with each one *A. senegal* and one *A. seyal* pool sample. Each of the pairs was mixed into 11 new samples, with a blend of 0%–100% *A. senegal* in *A. seyal* in 10% increments. This procedure resulted in 33 mixtures that were then measured using NIR spectroscopy as described above.

3. Theory

In experiment 1, principal component analysis (PCA) (S. Wold, Esbensen, & Geladi, 1987) was used to gauge if it was possible to distinguish between the two species. PCA is the most widely applied linear projection method for unsupervised exploratory multivariate data analysis. It is often used in data analysis for class detection as its ability to visualize the similarities and differences between the spectra including outlier detection. The basic objective of PCA is to extract lower dimensional orthogonal variables, principal components or latent variables, from a large number of original correlated variables. These components describe, in decreasing order, the maximum variance of original data. PCA decomposes the original data X (the NIR spectra) as

$$X = TP^T + E \quad (1)$$

where T, the scores matrix, represents the information of the projected data, and the loadings matrix P corresponds to the variables contribution. E contains the residual variation (non-systematic information) not captured by the model.

The partial least squares (PLS) regression used in experiments 2 is a powerful and arguably the most widely used method for supervised quantitative analysis (Haaland & Thomas, 1988). PLS builds up a linear regression mode between predictor matrix X and target matrix Y. PLS not only finds a smaller subspace explaining the maximum amount of variation in X as PCA does, but also ensure the coordinates of the new subspace that describe the response vector Y well. Thus, PLS decomposes both matrices into several latent variables, explaining maximum variations of X and Y. In PLS, y is correlated with X as (Svante Wold, Sjöström, & Eriksson, 2001)