Identifying type of sugar adulterants in honey: Combined application of NMR spectroscopy and supervised machine learning classification

Kavitha Rachineni [a,**], Veera Mohana Rao Kakita [c,1], Neeraj Praphulla Awasthi [a], Vrushali Siddesh Shirke [a], Ramakrishna V. Hosur [c], Satish Chandra Shukla [b,*]

[a] *Export Inspection Agency – Mumbai, E-3, Industrial Area (MIDC), Andheri East, Mumbai, 400 093, India*
[b] *Export Inspection Agency- Chennai (Head Office), 6th Floor CMDA Tower-II, No: 1 Gandhi Irwin Road, Egmore, Chennai, 600008, India*
[c] *UM-DAE Centre for Excellence in Basic Sciences, University of Mumbai, Kalina Campus, Santacruz, Mumbai, 400 098, India*

ARTICLE INFO

ABSTRACT

Nuclear magnetic resonance (NMR) is a powerful analytical tool which can be used for authenticating honey, at chemical constituent levels by enabling identification and quantification of the spectral patterns. However, it is still challenging, as it may be a person-centric analysis or a time-consuming process to analyze many honey samples in a limited time. Hence, automating the NMR spectral analysis of honey with the supervised machine learning models accelerates the analysis process and especially food chemistry researcher or food industry with non-NMR experts would benefit immensely from such advancements. Here, we have successfully demonstrated this technology by considering three major sugar adulterants, i.e., brown rice syrup, corn syrup, and jaggery syrup, in honey at varying concentrations. The necessary supervised machine learning classification analysis is performed by using logistic regression, deep learning-based neural network, and light gradient boosting machines schemes.

1. Introduction

Honey is a most valued natural sweetener produced by honey bees and is composed of several sugars, varied compositions of organic acids, amino acids, enzymes, and minerals (Missio da Silva et al., 2016). The therapeutic and nutritional value of honey is known to be significant, and that has increased its consumption among people. However, unfortunately, honey is also observed to be one of the most adulterated foods (Fakhlaei et al., 2020). In honey, the possible adulterations are of many types, which include, deliberate addition of C4 (corn/cane sugars), C3 (rice syrups), and invert sugars. Often, feeding sugars to honey bees in off-seasons, fermentation caused due to improper storage conditions, and sometimes processing also cause changes in the chemical constituent proportions. Thus, adulterations damage the authentic benefits of honey. Therefore, there is a significant demand for screening the authenticity of honey using various analytical chemistry tools and many analytical tools have been used (Tura and Seboka, 2020; Zábrodská and Vorlová, 2015; Consonni and Cagliani, 2015; Elflein and

Raezke, 2008). Among them, NMR is considered one of the vital and non-destructive spectroscopic tools useful to monitor the authenticity of honey (Olawode et al., 2018; Machado et al., 2020; Ohmenhaeuser et al., 2013; Spiteria et al., 2015; Lolli et al., 2008).

Melissopalynology (microscopic study of pollen grains) and some physicochemical parameters such as sugar content, concentrations of proline, HMF, free acids, and diastase activity are some of the traditional methods for determining honey quality; however, a set of parameters must be considered to draw a decision on honey quality. The determination of these traditional characteristics is operator-dependent. Whereas, IRMS (isotopic ratio mass spectroscopy) is a sophisticated analytical technique that uses carbon isotope ratios to detect adulterations in honey. In general, its hyphenated approaches, EA-IRMS (elemental analysis coupled IRMS) and LC-IRMS (liquid chromatography coupled IRMS), can be used to evaluate honey with extractable proteins; however, these schemes have recently been extended to analyze honey with non-extractable proteins (Dong et al., 2018). IRMS, on the other hand, indirectly detects C3 sugar adulterants and can also

be time-consuming. Conversely, honey analysis from NMR spectroscopy requires less sample preparation and data collection times when compared with other analytical methods.

The inherent strength of NMR (target and non-target based) permits identification and quantification of all possible monosaccharides, disaccharides, oligosaccharides, acids, HMF, and amino-acids, separately from different well-resolved chemical shifts. These features can be easily exploited to discriminate geographical and botanical origins of honey since each honey variety has its unique NMR spectral features/signatures (Girelli et al., 2020; Spiteri et al., 2020; Boffo et al., 2012; Ribeiro et al., 2014; Nguyen et al., 2017; Luong et al., 2019; Pu'scion-Jakubik et al., 2020). Thus, to detect the authenticity of honey under testing, a specific honey NMR database with the respective authentic honey samples is required. Even so, often, these honey NMR databases of authentic samples fail to provide specific insights into the type of adulteration that has taken place. Previously, in one of the reports, NMR combined with statistical analysis has been used to identify the commercial sugar syrup adulterations in honey (which are routinely used as nutrition to bees) (Bertelli et al., 2010). In another work, brown rice syrup adulterated honey has also been discriminated from authentic honey, while considering only one specific ^{1}H chemical shift peak at 5.39 ppm (Musharraf et al., 2016). Still, simultaneously and rapidly classifying several sugar syrup adulterations in a large group of honey samples is rather challenging; this is particularly relevant in an industrial environment, where a large number of samples have to be tested reliably.

In the present work, we have demonstrated the strength of NMR in combination with supervised machine learning strategies for classifying honey samples with three different sugar syrup adulterations. In this context, different direct, intentional adulterations are considered by adding varying concentrations of sugar sugars such as corn syrup, brown rice syrup, jaggery syrup to a set of authentic Indian rapeseed honey samples. Subsequently, statistical analysis through various supervised machine learning techniques of the NMR spectra has been done to get insights into the kind of adulteration that has taken place.

2. Materials and sample preparation

Indian rapeseed honey samples, corn syrup, brown rice syrup, and jaggery syrup used in the present study are taken in a petri dish kept in an oven at 50 °C for about 20 min to homogenize the honey samples. After that, samples are weighed to 2.5 g in a 15 ml polypropylene tube (required concentrations (w/w) of adulterations are calculated and weighed). After weighing, the sample volumes are adjusted to 10 ml. These samples are vortexed properly for about 20 min. Then the samples are centrifuged at 6000 RPM for about 30 min. Later 900 µl of sample solutions are pipetted out in cryovials, and 100 µl of 1 M KH_2PO_4 in D_2O buffer having 0.05% of TSP as an internal reference standard is added, and finally, pH is adjusted to 3.1 (Bruker BTpH unit), which aids in reproducing the NMR spectral results (to eliminate the effect of sample pH changes on NMR chemical shifts). From that, 600 µl of pH adjusted samples are pipetted out into 5 mm NMR tubes for the NMR data acquisition (Ohmenhaeuser et al., 2013; Spiteria et al., 2015; Lolli et al., 2008).

A total of 20 Indian rapeseed honey, 14 corn syrup adulterated honey, 14 brown rice syrup adulterated honey, and 11 jaggery syrup adulterated honey samples are prepared under an identical sample preparation procedure. All the adulterant concentrations are ranging from ~5% to ~30% w/w with respect to the authentic Indian rapeseed honey (for all the adulterant spectra illustrating the percentages, see supporting information Table S1).

3. NMR experimental procedure

For all the honey samples, pre-saturated proton 1D-NOESY (Mckay, 2011) NMR spectra were recorded under identical experimental

parameters on a Bruker 400 MHz AVANCE NEO spectrometer equipped with a room temperature BBI probe. The offset is set to 4.702 ppm, with water peak suppression. Overall, recording 65,536 data points with a spectral width of 20.5 ppm resulted in a 4 s of FID length (acquisition time), and 32 scans are recorded for each sample (for the complete data acquisition parameters, see supporting information Table S2). Then, the Fourier transformed (data processing parameters are given in supporting information Table S3) NMR spectra were used for the statistical analysis by machine learning methods to discriminate the adulterated honey, i. e., brown rice adulterated, corn adulterated, and jaggery adulterated honey from the pure Indian rapeseed honey.

4. Results and discussion

4.1. NMR spectral analysis

Fig. 1 compares the representative 1D-NMR spectral features of Indian rapeseed honey, and the adulterated samples, i.e., corn, brown rice, and jaggery adulterated honey samples. The aliphatic region (0–3 ppm, Fig. 1a) consists of leucine, ethanol, proline, succinic acid, acetic acid, alanine, malic acid, citric acid, and many more (Soares et al., 2017) Herein, ethanol, succinic acid, and acetic acid are the fermentation markers of honey (Sroka and Tuszyński, 2007; Mărgăoan et al., 2020). Some of the other constituents, alanine, leucine, proline, citric acid, and malic acid are the geographical indicators. Whereas, the expanded chemical shift region from 3 to 5.3 ppm (Fig. 1b) mainly consists of fructose and glucose resonances with high intensities (sum of glucose and fructose is > 60 g/100 g of honey) when compared with the other chemical shift regions. Further, these NMR spectral features are most common among all the three adulterants and pure honey; hence, clear-cut discrimination cannot directly be done from this spectral region.

Interestingly, in the chemical shift region from 5.3 to 5.5 ppm (Fig. 1c), significant differences in the NMR spectral patterns are observed among all the samples, which is mainly due to the presence of disaccharides, trisaccharides, and oligosaccharides (Schievano et al., 2017) Composition of these saccharides are very specific to the adulterated honey and authentic honey samples. As a consequence, from the given expanded spectra, it is evident that the increased peak intensities of maltose and the other higher oligosaccharides have made the peak appearance different for both the corn and brown rice adulterated honey from the authentic rapeseed honey spectrum. Whereas, in the jaggery adulterated honey, increased sucrose peak intensities can facilitate its discrimination from the authentic and two other adulterations (corn and brown rice adulterated honey). Hence, only this small chemical shift region is considered for the present supervised machine learning classification task.

The chemical shift region from 5.5 to 10.5 ppm (Fig. 1d) consists of signals belonging to tyrosine, phenylalanine, formic acid and 5-hydroxymethylfurfural (HMF). This region can be used to identify the geographical origin. Herein, the quality of honey can be assessed from the concentration of HMF. In general, higher concentrations (>80 mg/1 kg) of HMF signifies shortcomings in the quality of honey, which could be due to improper storage, overheating of honey in the processing, and the addition of invert sugars.

The power of NMR lies in the fact that a small section of the NMR spectrum, covering chemical shift range (5.3–5.5 ppm) alone can discriminate adulterations when coupled with supervised machine learning methods. The supporting information Table S4 provides a list of data analysis software.

4.2. Supervised machine learning

Supervised classification algorithms have been successfully demonstrated to classify varieties of datasets (with target labels); wherein, feature variables of samples are related through complex mathematical
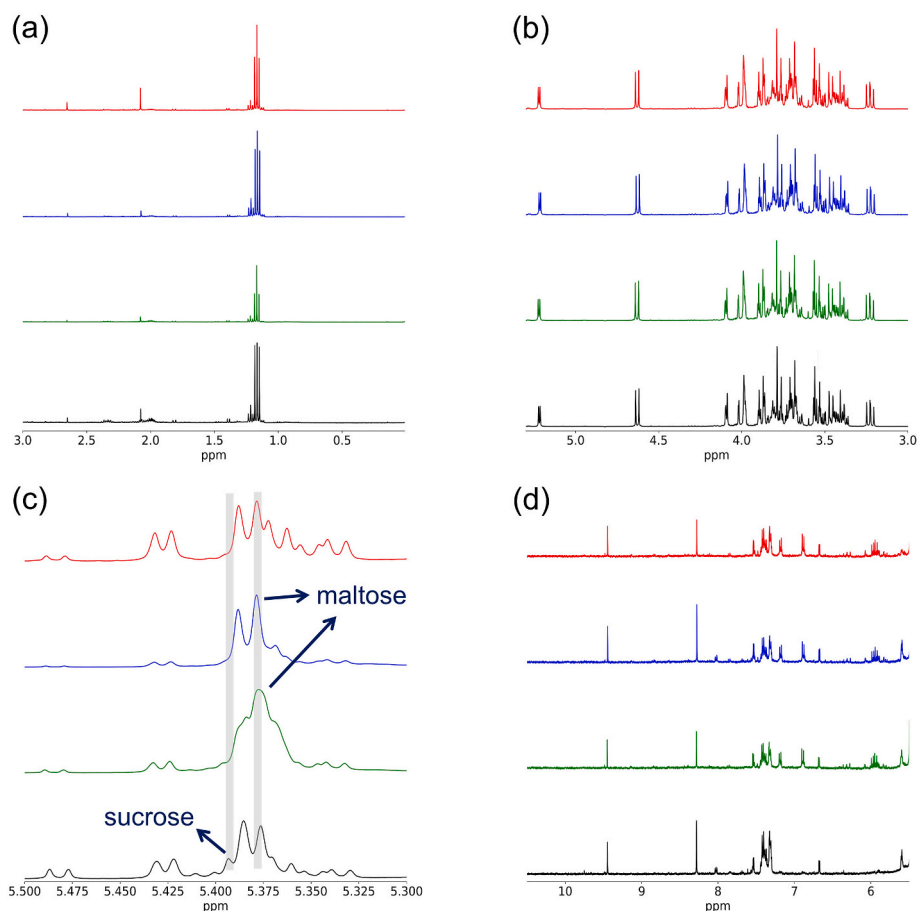
Fig. 1. Comparison of the expanded chemical shift regions of authentic Indian rapeseed honey (red), brown rice syrup adulterated honey (blue), corn syrup adulterated honey (green), and jaggery adulterated honey (black). See main text for the full details. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

expressions. Hence, in the present study, as the NMR spectra are found to be very complex, we believe that the supervised classification machine learning methods can also be used to classify the different adulterated honey samples. In any statistical analysis, in general, choosing only one of the algorithms randomly for the required classification task is not appropriate. To achieve reliability in the predictions, considering a set of supervised learning algorithms and evaluating their performance to solve the classification task of metabolite samples is necessary. After that, predicted classification results from these models can be further refined (through consolidating) by the voting classification technique (a target that has been predicted for the maximum times from all the supervised classification schemes).

In the present study, for the honey NMR classification task, we have considered three supervised classification schemes. This includes, (i) one of the widely used logistic regression classifier (Juliana and William, 2016), (ii) an advanced deep learning neural network classifier (DNN, Deng and Yu, 2014), and (iii) an ensemble-based light gradient boosting machine (LGBM, Ke et al., 2017) classifier. These selected statistical algorithms can learn differently from the sample features, as the working principles and mathematics behind the chosen models are distinct. Hence, subjecting all the models to the voting technique improves the classification performance. It is also worth noting that deep learning and other machine learning approaches have recently been successful in various food-related spectroscopic data analysis (Zhu et al., 2021; Zheng et al., 2014; Feng et al., 2021; Wang et al., 2021; Liang et al., 2020; Yan et al., 2021; He et al., 2021); thus, we expect that the considered machine learning and deep learning methods will work-well in the classification of various adulterant honey samples using NMR spectroscopy in
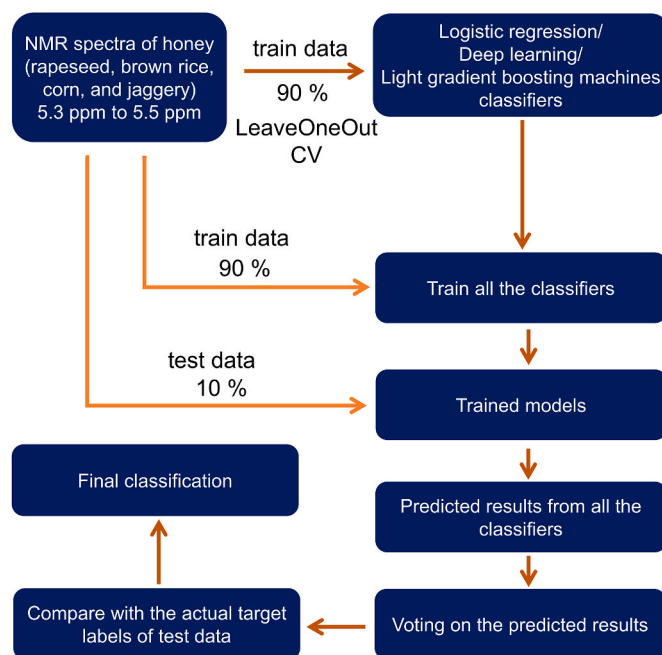

Fig. 2. Schematic representation of the complete classification procedure used in the present study. This routine has been repeated 50 times to avoid the bias associated with the train-test dataset splitting.

the proposed context as well. As schematically shown in Fig. 2, NMR spectra of 59 samples are used for supervised classification which includes 20 pure Indian rapeseed, 14 corn adulterated honey, 14 rice adulterated, and 11 jaggery adulterated honey samples with their targeted labels. As has been discussed above (Fig. 1c), the promising spectral region, 5.3–5.5 ppm of the 59 spectra is considered for the statistical analysis; the NMR input consists of peak positions (ppm) and intensities of the peaks. Then, the NMR spectral dataset (59 samples) has been randomly split into the training dataset (90%, 53 samples) and the testing dataset (10%, 6 samples). The training dataset has been used to train all the selected models, logistic regression, deep neural networks (DNN), and light gradient boosting machine (LGBM) classifiers. The performance of each model has been evaluated by using LeaveOneOut (LOO) cross-validation procedure. During this LOO, in each step, only one of the samples (one out of 53 samples) is used to validate the model, and the training procedure for the cross-validation is repeated as many times as the number of training samples (53 times with 52 training samples and one validation sample). The predicted LOO cross-validation accuracy (for each model) is known as the Q^2 score. However, models developed for the cross-validation cannot be used on the testing dataset, since in each step, the LOO procedure has resulted in a total of 53 trained models for each classifier. Therefore, all the said classifiers have been further retrained on the full training honey dataset (53 samples). Then, these trained classification models are ready to predict the honey target labels of the test dataset (6 samples). In order to consolidate the predicted target labels from all the classifiers, voting classification has been implemented and a comparison of the obtained voting labels with the actual target labels of the test dataset facilitates accuracy measurements. The whole routine given in Fig. 2 has been repeated 50 times (50 trials with different combination of 6 test samples) in a randomized sampling fashion, which avoids bias associated with the splitting of train and test datasets. Finally, the obtained Q^2 and accuracies from all the trials are averaged; herein, the models which have average Q^2 value and average accuracy value nearer to 1.0 and 100%, respectively, are the best performing classifiers.

The supervised classifiers used in the present study are schematically represented in Fig. 3. The technical details of these logistic regression, DNN, and LGBM classification algorithms can be found in the given references (Juliana and William, 2016; Deng and Yu, 2014; Ke et al., 2017). For completeness, we have given here only a brief description.

The logistic regression classifier (Fig. 3a) utilizes the one vs rest classification phenomenon in multiclass classification tasks. It is one of the simplest known classification techniques, wherein the sigmoid function is used to fit the sample features. In the present case, to minimize the overfitting L2 regularization is used. The obtained Q^2 average score is 0.97 over 50 trials of train-test dataset random sampling splits (for the parameters used, see supporting information Table S5).

Next, advanced supervised deep neural networks (DNN) classification (Fig. 3b) models are also considered for the classification of honey adulterations. Wherein, the number of input layers in the DNN is equal to the number of data points in the NMR spectra. Subsequently, hidden layers are added with a different number of units (ReLu activation function). The final output layer has as many units equal to the number of honey classes while using the softmax multi-class activation function. In this scheme, a dropout of 20% is used to overcome the overfitting issues associated with the DNN. For the cross-validation, as has been used for the conventional logistic regression, the LeaveOneOut scheme is implemented, while using the categorical cross-entropy for calculating the loss in cross-validation with the Adam optimizer. The resultant average value of Q^2 score value is equal to 0.99 over 50 trials of train-test dataset splits (for the parameters used, see supporting information Table S6).

The light gradient boosting machine (LGBM) (Fig. 3c) is an ensemble classifier, which has been first proposed by Microsoft and it oftentimes outperforms many of the deep learning schemes as well. The required training time for this LGBM is also very little when compared with the other ensemble methods and deep learning schemes. In the LGBM, gradient boosting trees is used as weak learners and a continuous summed score is assigned to each leaf for the predictions. In the present study, to avoid overfitting issues, all the hyper parameters are tuned and it is found that the gradient boosting decision trees has resulted in a better Q^2 score while using a learning rate of 0.1 (with the number of iterations equal to 100). The obtained average Q^2 score is 0.97 over 50 trials of train-test dataset splits (for the parameters used, see supporting information Table S7).

The obtained average Q^2 scores from all the models are very nearer to 1.0; hence, we can conclude that the selected supervised models are well-suited for the honey classification. In each step of the test-train dataset random sampling, after completing the LOO cross-validation procedure, the final supervised models are also developed by utilizing
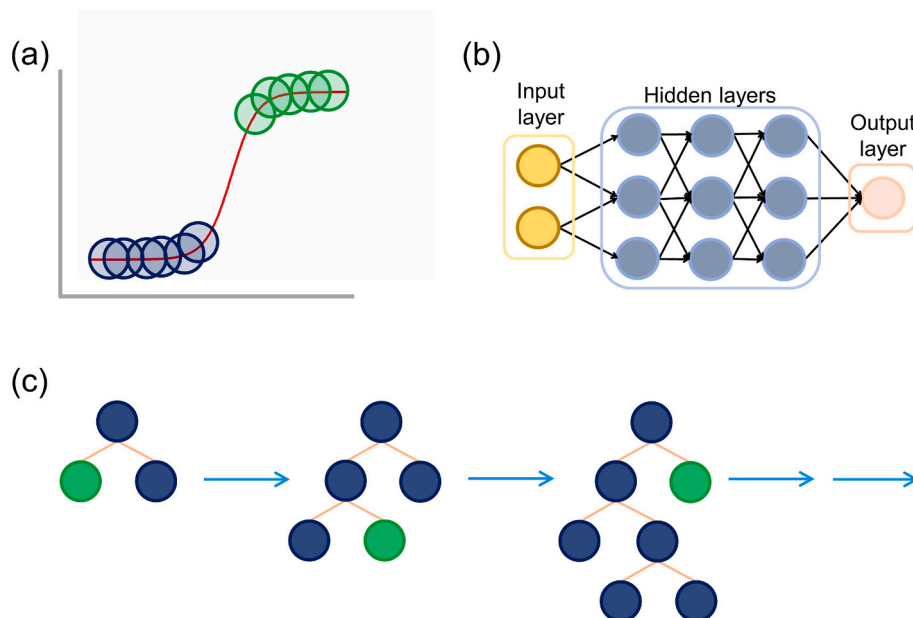

Fig. 3. Schematic representation of logistic regression (a), deep neural network (b), and light gradient boosting machine (c) classifiers.

the entire training dataset (53 samples), and the trained models (for three classifiers) are ready to predict the samples in the test dataset (6 samples, which are nowhere utilized for the model training or cross-validation). The model retraining has also been repeated 50 times (50 trials, on the training dataset obtained from a random sampling procedure), as in the cross-validation step. For clear understanding, out of 50 trials, predicted results obtained from three of the trials are compared in Fig. 4. In the first trial (Fig. 4a), explicit comparison of the predicted results and the target labels of the test honey dataset (sample-1: pure honey, sample-2: rice adulterated, sample-3: jaggery adulterated, sample-4: rice adulterated, sample-5: corn adulterated, sample-6: pure honey) has facilitated the measurement of classification accuracies. From the results, it is clear that for all the chosen classifiers, 100% accuracy is observed. These classification results from all the individual models on the test dataset of honey can be consolidated by using the voting method. The predictions from the voting method are compared with the actual test dataset of honey classes, in the first trial, which also has resulted in 100% accuracy. But there are some cases where predictions require voting methods, e.g., Fig. 4b, i.e., in the second trial, the test dataset has 6 samples (sample-1: pure honey, sample-2: jaggery adulterated, sample-3: corn adulterated, sample-4: rice adulterated, sample-5: pure honey, sample-6: rice adulterated), and the logistic regression and deep learning classifiers have predicted all the honey types correctly. Whereas, the LGBM classifier predicted sample-3 as rice adulterated honey instead of originally labelled corn adulterated honey sample. In this context, it is worthwhile to note that classification through the voting method is rather important; for the sample-3, in the second trial, the voting method (voting considers the sample label which has been predicted for maximum times from all the classifiers) correctly predicted the sample as corn adulterated honey label. Similarly, for the third trail (Fig. 4c), deep neural networks wrongly predicted sample-2 (original label: pure honey) and sample-3 (original label: pure honey) as rice adulterated honey; whereas, the other two remaining classifiers, logistic regression and LGBM, have correctly predicted all the sample labels. Hence, here too, the voting method has corrected the prediction errors associated with the individual classifiers. In the remaining trials also the voting method has played a role in accurately predicting the honey types. The obtained average accuracies over 50 trials are equal to 99.8%, 99.3%, and 98.7% respectively for the logistic regression, DNN and LGBM classifiers. Finally, assembling the results through voting (from all the classifiers) has resulted in 100% average accuracy.

5. Conclusions

Overall, the present work demonstrates the combined strength of NMR spectroscopy and supervised machine learning models to identify the different adulterations in honey samples, in an automatic fashion. Using 90% training and 10% testing data, the experimental 1D-NMR spectra of honey samples are subjected to three types of classification algorithms: logistic regression classifier, deep neural networks (DNN) classifier, and light gradient boosting machine (LGBM) classifier. In general, the DNN classifier requires a large amount of training data to achieve optimal performance in predicting target labels; however, because the experimental NMR data only has four different target labels as well as the spectra are rather distinct from one class of adulteration to the next, the working performance of considered DNN classifier model is good even with the small amounts of data. Further, the voting mechanism is used to combine the predictions from the three classifiers and the accuracies of the trained models are measured using these voting-based predictions. To reduce the bias associated with during the splitting of training and testing datasets, the entire cross-validation and predictions on the three classifiers are repeated 50 times. Finally, the average of the cross-validation score and accuracies is calculated, yielding values close to 1.0 and 100%, respectively. Thus, the use of NMR in combination with supervised machine learning can successfully identify the adulteration that has occurred. Indeed, supervised machine learning and deep learning tools will have a substantial impact on identifying a variety of other types of adulterations, such as invert sugar adulterations and the addition of a mixture of sugar syrups to honey. Furthermore, when paired with NMR, supervised machine learning methods may be used to authenticate other food products such as oils, tea, spices and many others.

Authors statement

Kavitha Rachineni: Conceptualization, Methodology, Formal analysis, Writing – original draft. **Veera Mohana Rao Kakita**: Formal analysis, Writing – review & editing. **Neeraj Praphulla Awasthi**: Conceptualization, Validation, Investigation, Writing – review & editing. **Vrushali Siddesh Shirke**: Investigation. **Ramakrishna V Hosur**: Formal analysis, Writing – review & editing. **Satish Chandra Shukla**: Supervision, Final Review & Guidance.
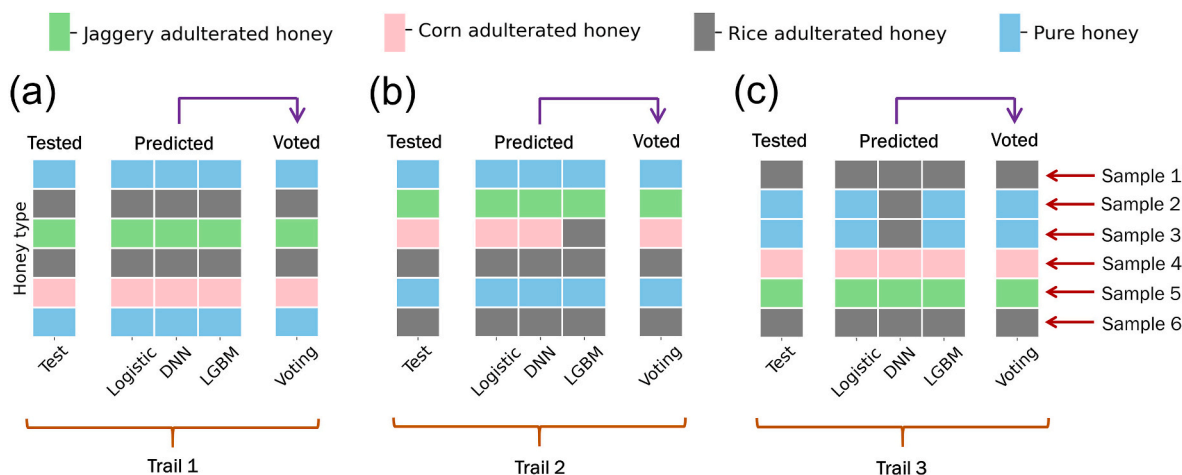

Fig. 4. Comparison of randomly sampled test datasets (3 trails from a total of 50 trails) to the predicted results from logistic regression, deep neural networks, light gradient boosting machine (LGBM) classifiers and the voting resultant labels from all the said models. Here, in each trail a total of 6 samples are used. The rectangular color boxes, green, pink, gray, and blue, respectively, represent jaggery adulterated, corn adulterated, rice adulterated, and pure honey samples. In all the trails, the voting method has resulted in highly accurate classification labels (see main text for the full details). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.crfs.2022.01.008.

References

Bertelli, D., Lolli, M., Papotti, G., Bortolotti, L., Serra, G., Plessi, M., 2010. Detection of honey adulteration by sugar syrups using one-dimensional and two-dimensional high-resolution nuclear magnetic resonance. J. Agric. Food Chem. 58, 8495–8501.

Boffo, E.F., Tavares, L.A., Tobias, A.C.T., Ferreira, M.M.C., Ferreira, A.G., 2012. Identification of components of Brazilian honey by 1H NMR and classification of its botanical origin by chemometric methods. LWT 49, 55–63.

Consonni, R., Cagliani, L.R., 2015. Recent developments in honey characterization. RSC Adv. 5, 59696–59714.

Deng, L., Yu, D., 2014. Deep learning: methods and applications. Foundation. Trend. Sign. Process. 7, 1–199.

Dong, H., Xiao, K., Xian, Y., Wu, Y., 2018. Authenticity determination of honeys with non-extractable proteins by means of elemental analyzer (EA) and liquid chromatography (LC) coupled to isotope ratio mass spectroscopy (IRMS). Food Chem. 240, 717–724.

Elflein, L., Raezke, K.-P., 2008. Improved detection of honey adulteration by measuring differences between $^{13}C/^{12}C$ stable carbon isotope ratios of protein and sugar compounds with a combination of elemental analyzer — isotope ratio mass spectrometry and liquid chromatography — isotope ratio mass spectrometry ($\delta^{13}C$-EA/LC-IRMS). Apidologie 39, 574–587.

Fakhlaei, R., Selamat, J., Khatib, A., Razis, A.F.A., Sukor, R., Ahmad, S., Babadi, A.A., 2020. The toxic impact of honey adulteration: a review. Foods 9, 1538.

Feng, L., Wu, B., Zhu, S., He, Y., Zhang, C., 2021. Application of visible/infrared spectroscopy and hyperspectral imaging with machine learning techniques for identifying food varieties and geographical origins. Front. Nutrit. 8, 680357. Article.

Girelli, C.R., Schiavone, R., Vilella, S., Fanizzi, F., 2020. Salento honey (apulia, southeast Italy): a preliminary characterization by ^{1}H-NMR metabolomic fingerprinting. Sustainability 12, 5009.

He, W., He, H., Wang, F., Wang, S., Lyu, R., 2021. Non-destructive detection and recognition of pesticide residues on garlic chive (Allium tuberosum) leaves based on short wave infrared hyperspectral imaging and one-dimensional convolutional neural network. J Food Measure. Character. 15, 4497–4507.

Juliana, T., William, J.M., 2016. Logistic regression relating patient characteristics to outcomes. JAMA 316, 533–534.

Ke, G., Meng, Q., Finley, T., Wang, T., Chen, W., Ma, W., Ye, Q., Liu, T., 2017. LightGBM: a highly efficient gradient boosting decision tree. In: 31st Conference on Neural Information Processing Systems, Long Beach, CA, USA.

Liang, N., Sun, S., Zhang, C., He, Y., Qiu, Z., 2020. Advances in infrared spectroscopy combined with artificial neural network for the authentication and traceability of food, Critical Reviews in Food Science and Nutrition. https://doi.org/10.1080/10408398.2020.1862045.

Lolli, M., Bertelli, D., Plessi, M., Sabatini, A.G., Restani, C., 2008. Classification of Italian honeys by 2D HR-NMR. J. Agric. Food Chem. 56, 298–1304.

Luong, D.V., Tam, N.Q., Xuan, D.T.T., Tai, N.T., 2019. NMR based metabolomic approach for evaluation of Vietnamese honey. Viet. J. Chem. 57, 712–716.

Machado, A.M., Miguel, M.G., Vilas-Boas, M., Figueiredo, A.C., 2020. Honey volatiles as a fingerprint for botanical origin—a review on their occurrence on monofloral honeys. Molecules 25, 374.

Mărgăoan, R., Cornea-Cipcigan, M., Topal, E., Kösoğlu, M., 2020. Impact of fermentation processes on the bioactive profile and health-promoting properties of bee bread, mead and honey vinegar. Processes 8, 1081.

Mckay, R.T., 2011. How the 1D-NOESY suppresses solvent signal in metabonomics NMR spectroscopy: an examination of the pulse sequence components and evolution. Concepts Magn. Reson. 38A, 197–220.

Missio da Silva, P., Gauche, C., Gonzaga, L.V., Costa, A.C.O., Fett, R., 2016. Honey: chemical composition, stability and authenticity. Food Chem. 196, 309–323.

Musharraf, S.G., Fatima, S.A., Siddiqui, A.J., Choudhary, M.I., Rahman, A., 2016. ^{1}H-NMR fingerprinting of brown rice syrup as a common adulterant in honey. Anal. Methods 8, 6444–6451.

Nguyen, T.A., Vu, T.G., Nguyen, T.L., Pham, Q.T., Ta, T.T., 2017. Classification and identification of Vietnamese honey using chemometrics based on 1H-NMR data. Viet. J. Sci. Technol. Eng. 59, 14–21.

Ohmenhaeuser, M., Monakhova, Y.B., Kuballa, T., Lachenmeier, D.W., 2013. Qualitative and quantitative control of honeys using NMR spectroscopy and chemometrics. Int. Scholar. Res. Notice. 9, 825318.

Olawode, E.O., Tandlich, R., Cambray, G., 2018. ^{1}H-NMR profiling and chemometric analysis of selected honeys from South Africa, Zambia, and Slovakia. Molecules 23, 578.

Puścion-Jakubik, A., Borawska, M.H., Socha, K., 2020. Modern methods for assessing the quality of bee honey and botanical origin identification. Foods 9, 1028.

Ribeiro, R.d.O.R., Mársico, E.T., Carneiro, C.d.S., Monteiro, M.L.G., Júnior, C.C., Jesus, E.F. O.d., 2014. Detection of honey adulteration of high fructose corn syrup by Low Field Nuclear Magnetic Resonance (LF 1H NMR). J. Food Eng. 135, 39–43.

Schievano, E., Tonoli, M., Rastrelli, F., 2017. NMR quantification of carbohydrates in complex mixtures. A challenge on honey. Anal. Chem. 89 (24), 13405–13414.

Soares, S., Amaral, J.S., Oliveira, M.B.P.P., Mafra, I., 2017. A comprehensive review on the main honey authentication issues: production and origin. Compr. Rev. Food Sci. Food Saf. 16, 1072–1100.

Spiteri, C., Lia, F., Farrugia, C., 2020. Determination of the geographical origin of Maltese honey using 1H NMR fingerprinting. Foods 9, 1455.

Spiteria, M., Jamina, E., Thomasa, F., Reboursa, A., Leesa, M., Rogersb, K.M., Rutledgec, D.N., 2015. Fast and global authenticity screening of honey using 1H-NMR profiling. Food Chem. 189, 60–66.

Sroka, P., Tuszyński, T., 2007. Changes in organic acid contents during mead wort fermentation. Food Chem. 104, 1250–1257.

Tura, A.G., Seboka, D.B., 2020. Review on honey adulteration and detection of adulterants in honey. Int. J. Gastroenterol. 4, 1–6.

Wang, L., Li, J., Li, T., Liu, H., Wang, Y., 2021. Method superior to traditional spectral identification: FT-NIR two-dimensional correlation spectroscopy combined with deep learning to identify the shelf life of fresh phlebopus portentosus. ACS Omega 6, 19665–19674.

Yan, S., Wang, S., Qiu, J., Li, M., Li, D., Xu, D., Li, D., Liu, Q., 2021. Raman spectroscopy combined with machine learning for rapid detection of food-borne pathogens at the single-cell level. Talanta 226, 122195.

Zábrodská, B., Vorlová, L., 2015. Adulteration of honey and available methods for detection – a review. Acta Vet. 83, 85–102.

Zheng, W., Fu, X., Ying, Y., 2014. Spectroscopy-based food classification with extreme learning machine. Chemometr. Intell. Lab. Syst. 139, 42–47.

Zhu, L., Spachos, P., Pensini, E., Plataniotis, K.N., 2021. Deep learning and machine vision for food processing: a survey. Curr. Res. Food Sci. 4, 233–249.