Handheld Raman for rapid screening for oil type used in potato chip manufacturing

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ABSTRACT

Oil is a key ingredient in potato chip manufacturing serving as heat transfer agent and providing flavor and texture. As the trend toward wellness keeps gaining strength, selection of oils can add value as healthier alternatives. Adulteration of high-price oils is a prevalent source of agricultural fraud. There is a need for reliable methods to detect oil misclassification or economically-motivated adulteration. Our objective was to develop rapid detection method to identify the type of oil used in manufacturing of potato chips and to predict the fatty acid profile of the oil based on the unique Raman spectral patterns. Our data showed that 60% of potato chips were manufactured with single oils including corn (20%), canola (8%), sunflower (18%), peanut (6%), safflower (1%) and cottonseed (7%) oils. The Raman fingerprints from oils allowed to form tight clustering of samples based on type of oil allowing excellent sensitivity and selectivity using an independent set of samples. Based on the prediction of SIMCA, 15% of potato chips were misclassified oil source on their label. In addition, the spectra allowed to predict the main fatty acids (oleic and linoleic acid) with strong correlation (Rval>0.96) and low standard error of prediction. The Raman models obtained from two handheld instruments equipped with 1064nm and 785 nm excitation laser matched the result perfectly with each other and they both had their own advantage in specific application conditions. Overall, the handheld Raman technology provides an effective tool to rapidly and in-situ identification of oil type of potato chips in the market.

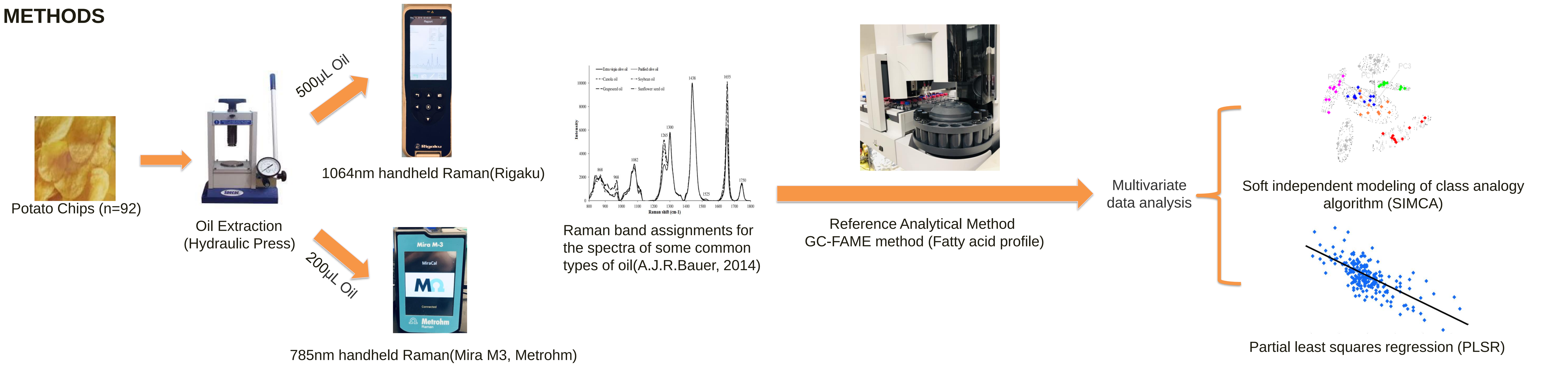
INTRODUCTION

- The global potato chips market size reached US$ 29 Billion in 2018, and it is projected to reach US$ 35 Billion by 2024.
- Oil is a significant component in potato chips.
  - Oil content in potato chips is usually between 35% and 44%.
  - Heat transfer agent and providing flavor and texture. 60 of the approximately 150 volatile compounds identified come mainly from lipid degradation, with the polyunsaturated fatty acids of the frying oil likely to be their main precursors (Martin & Ames, 2001).
- The common types of oil which are utilized in potato chip manufacturing are corn, canola, sunflower, high oleic(HO) safflower and cottonseed oils (Aykas & Rodriguez-Saona, 2016).
- Edible oils and fats are one of the most counterfeited foods in the industry.
  - Making healthier potato chips depends upon the oil type when cooking the chips.
  - Canola, soybean, and palm oils are the common adulterants for high price oils.
- The traditional analytical method (GC-FAME) of oil is time-consuming, labor-intensive and it has a limitation in the in-field application and detection.
- Handheld Raman devices can be taken or placed at- or in-line to points of vulnerability along complex food supply networks.
  - Measure sample through transparent packaging (less sample preparation) and screen a larger number of samples.

OBJECTIVE

- To develop a rapid detection method to identify the type of oil used in manufacturing of potato chips.
- To predict the fatty acid profile of the oil based on the unique Raman spectral patterns.

METHODS



RESULTS

Table 1.Fatty acid composition of the potato chips oils by GC-FAME method

Oil Type	Palmitic (%)	Stearic (%)	Oleic (%)	Linoleic (%)	Linolenic (%)
HO SUN	4.5	2.7	79.5	12.6	0.6
HO CAN	4.2	1.9	69.8	21.5	2.7
CAN	4.6	1.7	64.9	20.5	8.2
NUSUN	5.4	3.3	63.3	27.9	0.2
SAFF	6.1	2.9	74.7	15.8	0.5
PEANUT	8.2	2.3	45.5	43.3	0.7
CORN	11.9	1.7	30.4	55.1	1.0
COTTON	23.5	2.7	22.0	51.7	0.2

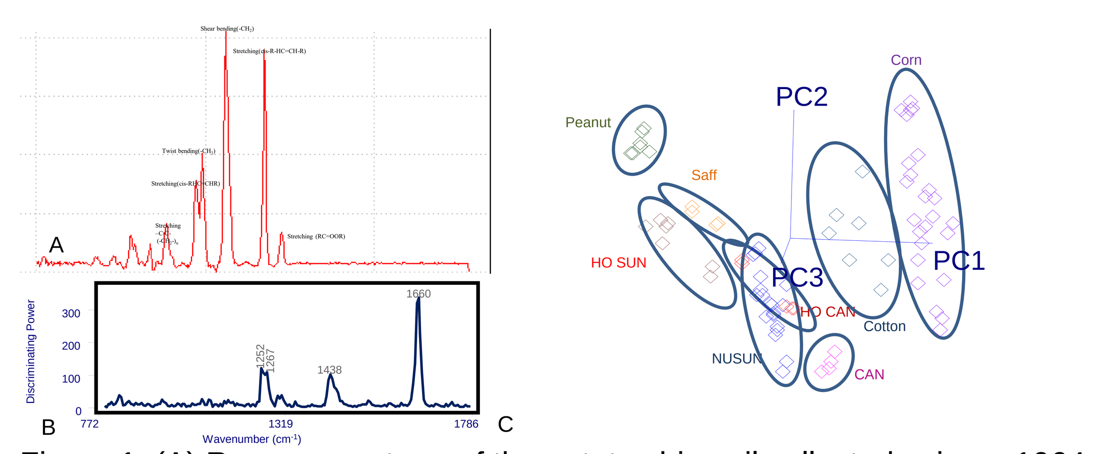
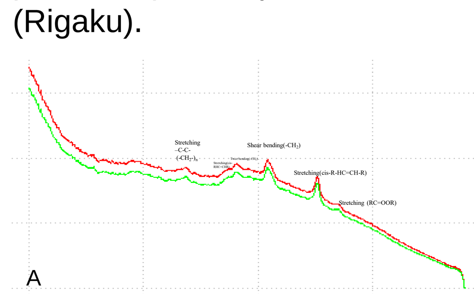


Figure 1. (A) Raman spectrum of the potato chips oil collected using a 1064nm excitation laser (Rigaku). (B)SIMCA discriminating plot based on the Raman spectra of potato chip oils using the Rigaku Raman. (C) Soft independent modeling of class analogy (SIMCA) 3D projection plots for authentication of potato chips' oil by handheld Raman equipped with 1064nm excitation laser (Rigaku).



	HO SUN	HO CAN	NUSUN	PEANUT	CORN	COTTON
HO SUN	0.0					
HO CAN	2.2	0.0				
NUSUN	3.7	1.7	0.0			
PEANUT	3.8	1.9	2.4	0.0		
CORN	5.1	2.8	3.4	1.9	0.0	
COTTON	5.1	3.3	3.7	2.5	2.3	0.0

B

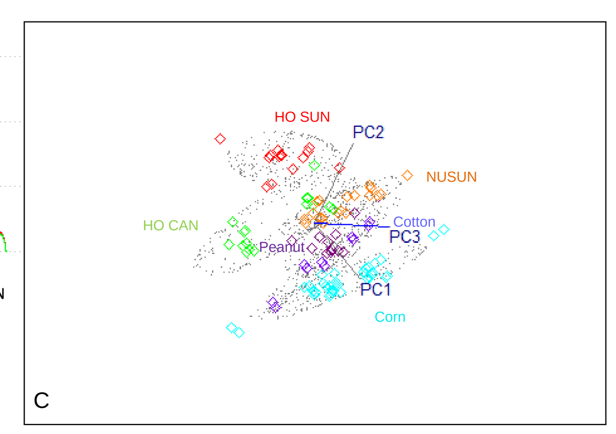


Figure 2. (A) Raman spectrum of the potato chips oil collected using a 785nm excitation laser (Mira M3, Metrohm). (B) Interclass distances between each type of oils based on GC-FAME and Raman analysis. (C) Soft independent modeling of class analogy (SIMCA) 3D projection plots for authentication of potato chips' oil by handheld Raman equipped with 785nm excitation laser (Mira M3, Metrohm).

Table 2. Prediction Performance Summary for fatty acids based on PLSR models using (A) 1064nm handheld Raman (Rigaku) and (B) 785nm handheld Raman(Mira M3, Metrohm)

A

Fatty Acids	Factor #	R Calibration	R Validation	SEC	SECV
Palmitic	6	0.95	0.90	1.37	2.01
Stearic	6	0.90	0.79	0.34	0.47
Oleic	4	0.98	0.97	3.86	4.57
Linoleic	4	0.99	0.98	2.72	3.23
Linolenic	7	0.98	0.94	0.31	0.58

B

Fatty Acids	Factor #	R Calibration	R Validation	SEC	SECV
Palmitic	6	0.94	0.90	1.95	2.45
Stearic	6	0.86	0.72	0.50	0.68
Oleic	4	0.97	0.97	4.18	4.83
Linoleic	4	0.97	0.96	3.87	4.37
Linolenic	7	0.90	0.77	0.60	0.88

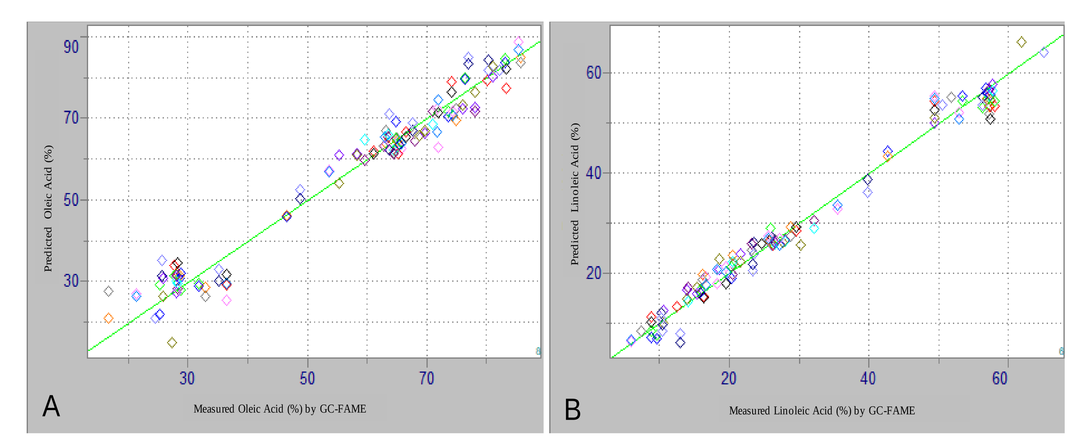


Figure 3. PLSR models of A: Oleic B: Linolenic Acid Percentage based on the data collected from GC FAME method and 1064nm handheld Raman(Rigaku).

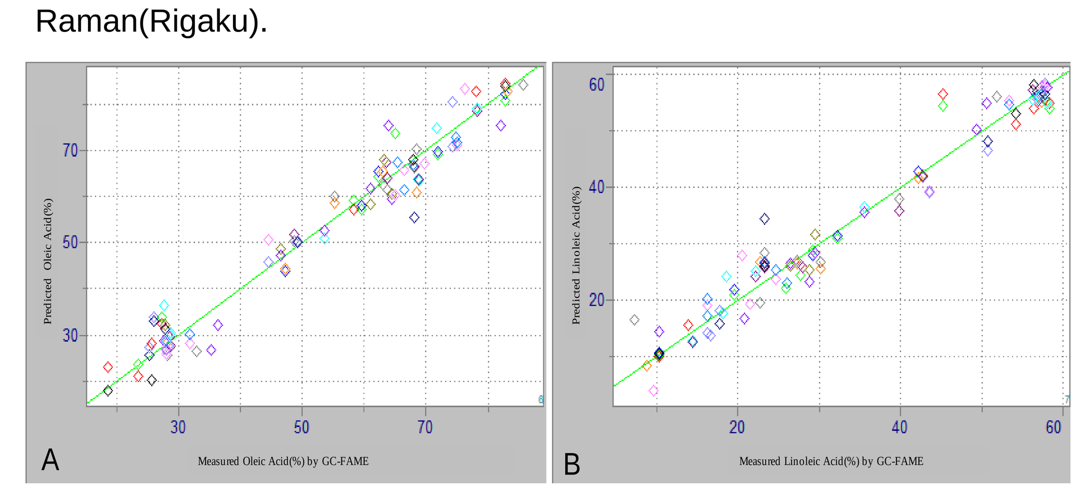


Figure 3. PLSR models of A: Oleic B: Linolenic Acid Percentage based on the data collected from GC FAME method and 785nm handheld Raman(Mira M3, Metrohm).

DISCUSSION

- Handheld Raman devices with 785nm and 1064nm excitation laser both are capable of rapidly classify the oil type used in the potato chips.
- The stretching(cis-R-HC=CH-R), shear bending(-CH_2), twist bending(-CH_2), and stretching(cis-RHC=CHR) were responsible for the successful separation in the SIMCA model.
- The Raman models matched perfectly the results from a portable FTIR unit equipped with a five reflection ATR crystal.
  - 60% of potato chips were manufactured with single oils including corn (20%), canola (8%), sunflower (18%), peanut (6%), safflower (1%) and cottonseed (7%) oils.
  - 15% of potato chips were misclassified oil source on their label.
- The spectra generated from two handheld Raman devices both allowed to predict the main fatty acids (oleic and linoleic acid) in the potato chips with strong correlation (Rval>0.96) and low standard error of prediction. The PLSR model generated from 1064nm handheld Raman data showed a better performance than 785nm.
- Because of the interference of fluorescence, the Mira M3 handheld Raman is limited in the application of potato chips with some types of seasoning and pigments. But for the applicable samples, it only requires 200 µL oil to finish the screening.
- The handheld Raman technology provides an effective tool to rapidly and in-situ identification of oil type of potato chips in the market.

SIGNIFICANCE

- Handheld Raman coupled with chemometrics generated robust, non-destructive and accurate algorithms to authenticate frying oils, requiring only few drops of sample (0.2~0.5 mL).
- This technology can substitute labor-intensive, time-consuming and hazardous reference methods used for oil-testing and assure the authenticity of our food supply.

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