# UNIVERSITI TEKNOLOGI MARA

# AUTHENTICATION OF HARUMANIS MANGO (*Mangifera Indica Linn.* cv MA128) USING CHROMATOGRAPHIC AND CHEMOMETRICS ANALYSIS OF VOLATILE ORGANIC COMPOUNDS (VOCS)

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# ABSTRACT

Harumanis mango (*Mangifera indica Linn.)* is highly valued for its exotic aroma and delicious taste. Due to its popularity, the price of Harumanis is high and make it becomes the target of economic adulteration involving substitution and misinterpretation. According to the Department of Agriculture (DOA), Tong Dam mango was often used to deceive consumers due to its almost identical physical characteristics to that of a Harumanis mango. Thus, a comprehensive tool is necessary for discriminating the authentic and unauthentic Harumanis mangoes whereby in this study a combination of three techniques, sensory analysis, chromatographic fingerprint, and chemometric techniques were explored. Using a simple duo-trio sensory test on 30 respondents, it revealed that only 57% of the respondents managed to differentiate Harumanis from the Tong Dam mangoes. On the other hand, the acceptance test conducted using the 9-point hedonic scale, demonstrated that the single significant parameter recorded was the aroma. Hence, the volatile organic compounds (VOCs) were selected as important criteria in this authentication study. HeadSpace / Solid Phase Microextraction (HS/SPME) method was chosen for the extraction of VOCs in mango samples. Optimization of HS/SPME parameters were achieved using two stages multivariate analysis; Plackett-Burman and response surface methodology (RSM) using Harumanis samples from orchards in Perlis. Optimum extraction temperature of 55 °C at 34 min extraction time gave linearity ranging from 100 – 500 µg/mL ($R^2$ = 0.9884 – 0.9936). The developed GC-MS method was used to obtain chromatographic fingerprint analysis on the authentic and unauthentic Harumanis samples. From the chromatographic fingerprints, 72 compounds with quality greater than 80% were identified. It was found that three ocimene compounds: beta ocimene, trans beta ocimene, and allo ocimene existed in all Harumanis mangoes regardless of their different sources (Perlis or Surabaya), while all these ocimene compounds did not appear in the unauthentic Harumanis volatile profile. This observation was further studied by chemometric techniques: cluster analysis (CA), discriminant analysis (DA), and principal component analysis (PCA) applied to 30 VOCs with peak areas as variables. The CA was able to classify the mango samples into two clusters; all authentic Harumanis samples from 21 locations in Perlis and Surabaya were grouped into one cluster, while the unauthentic samples from 13 locations were grouped into another cluster. The data sets achieved 100% correct classification for all the DA models. PCA successfully identified three ocimene compounds loadings along with beta-myrcene and heicosene as significant parameters that contributed to the discriminative tendencies of the mango samples. Further investigation on the significant compounds in the discrimination of authentic and unauthentic Harumanis mangoes using partial least squares-discriminant analysis (PLS-DA) showed that all three ocimene compounds provided variable importance in projection (VIP) score higher than 1.5, demonstrating these compounds as the chemical markers. On the other hand, on the quality control part, the effect of the chemical compounds' variation in different parts, origins and ripening stages were significant while the difference in harvesting years and grades recorded insignificant differences in the variation of chemical compounds. Thus, this work has successfully developed as a reliable tool in the authentication and quality control of Harumanis mango.

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# CHAPTER ONE
# INTRODUCTION

## 1.1 Background of Study

Agriculture is an essential sector with significant contributions to the economic growth and development of Malaysia. Being the economic pillar for this country, the agriculture sector has continuously produced agricultural products for both domestic and international uses. Agriculture has been recognised as one of the 12 National Key Economic Areas (NKEAs) and for its contributions to the country's gross domestic product (GDP). In 2018, the agriculture sector received the highest budget allocation, including grants and other state support for agriculture, food, and Halal industries. Under the Department of Agriculture (DOA), a special project known as entry point projects (EPP) was introduced for the export of top-quality fruits and vegetables from this country to the Middle East and European regions that are major importers of these fruits and vegetables (exceeding 50% of the global production of fruits and vegetables that meet the food safety standards) (Salaam, 2017). In general, Europeans have positive attitudes towards the consumption of tropical fruits, as they are convinced that tropical fruits are high in nutritive value, delicious, appealing, and rare (Sabbe et al., 2008).

Mango scientifically known as *Mangifera indica* L. is an essential tropical fruit that is fragrant and delicious. Mango represents the fourth largest tropical fruit industry worldwide and is highly in demand due to its appealing qualities—mangoes are generally succulent and nutritious (FAOSTAT, 2017). Mangoes are rich in carotenoids, ascorbic acids, quercetin, and mangiferin (Lauricella et al., 2017). At present, Asia, which accounts for 74.30% (34.6 million tons) of the global mango production, remains the largest mango producer globally. More than 500 fully characterised mango varieties in Asia are distributed worldwide (Lawson et al., 2019) but mangoes are mostly cultivated for domestic consumption (Kuhn et al., 2017). Thailand, India, Pakistan, China, Mexico, and Brazil are among the top mango producers (Laohaprasit, Kukreja, & Arunrat, 2012). To date, DOA has registered 77 mango varieties and 209 mango clones in Malaysia, including "Harumanis" (the most popular and expensive mango),