Iranian Food Science and Technology Research Journal
Vol. 18, No. 3, Aug. Sep. 2022, p. 31-51

نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد ۱۸، شماره ۳، مرداد - شهریور ۱۴۰۱، ص. ۵۱-۳۱

Homepage: http://ifstrj.um.ac.ir

Full Research Paper

Detection of adulterants and contaminants in black pepper, cumin, fennel, coriander and turmeric using GC-MS technique for forensic investigation

P. Choudhary[1], A. Seth[2], K. Lata Verma[3*]

Received: 2022.03.03
Accepted: 2022.04.18

How to cite this article:
Choudhary, P., Seth, A., Lata Verma, K. (2022). Detection of adulterants and contaminants in black pepper, cumin, fennel, coriander and turmeric using GC-MS technique for forensic investigation. *Iranian Food Science and Technology Research Journal*. 18 (3), 31-51.

Abstract

Forensic investigation is very crucial for identifying quality and safety issues related to food and its product. GC- MS has been used extensively in food analysis, and in the present study, it was used to identify the active constituents of some household spices as well as to detect the adulterants and contaminants which might be present in the samples. Spices used in the present study are black pepper, cumin, fennel, coriander and turmeric. The spice extracts were found to be useful in authenticating the spices by identifying various active constituents of the spices, like piperine, caryophyllene and 3- carene in black pepper; cuminaldehyde and 1, 3- methadien-7- al in cumin; anethole and fenchone in fennel; linalool, and geranyl vinyl ether in coriander and turmerone and zingiberene in turmeric. The adulterants detected qualitatively were plant- based adulterants. GC- MS is proved to be an effective tool in detecting plant- based adulterants, microbial contaminants, and agro chemical residues as well as industrial and manufacturing waste.

Keywords: GC-MS, Spice adulteration, Spice authentication, Spice contaminants, Qualitative.

Introduction

Spices are dried plant materials, which are usually used as a flavoring, coloring, or preservative agents in the foodstuff. They are used extensively all over the world for their culinary and medicinal properties (Attokaran, 2011). According to Food and Agriculture Organization (FAO), 28, 94,248 tons of spices were produced worldwide in the year 2019 and the major producer countries are India, China, Ethiopia, Indonesia, and Turkey (FAOSTAT, 2019). India is the spice bowl of the world, spices are used extensively in various Indian recipes and household remedies (Raghavan, 2006). India is the world's largest producer, consumer, and exporter of spices as it produces 75 of 109 varieties listed by International Organization for Standardization (ISO) and accounts for half of the global trading in spices (Indian trade portal, 2021). Spices are a very essential commodity; they are very important not only as food condiments but also have valuable medicinal properties (Attokaran, 2011; Raghavan, 2006). The global spice market was valued at 13.77 billion USD, in the year 2019 and will continue to grow in the future (Seasonings and Spices Market Size, 2020). As the global trade of spices is growing rapidly, spices are becoming very prone to fraudulence. Food fraud refers to the illegal tampering of

1 and 3. Regional Forensic Science Laboratory, Government of NCT of Delhi, Home Department, Chanakyapuri, New Delhi, 110021, India.
2. Department of Anthropology, University of Delhi, Delhi, 110007, India.
(Corresponding Author Email: kanak.dfsl@gmail.com)
DOI: 10.22067/IFSTRJ.2022.75621.1155

foodstuffs and materials for monetary gain. Food stuffs are considered fraudulent if it contains– (a) any foreign material which is responsible for health hazard, (b) does not have any useful ingredients, (c) inferior ingredients, substances which resemble the product but does not contains any essential compounds, (d) any decomposed or spoiled compounds which can be incorporated during production or processing or storage and (e) mislabeling i.e., providing false claims about the food product such as the origin of production, additives used, etc (Msagat, 2018). Economically motivated adulteration (EMA) is considered the most common practice of food fraud in the food industry. It is the fraudulent and intentional adulteration of food products to increase their market value or to reduce their production cost for financial purposes (Braden, 2014). Spices and their products are often sold in bulk and loose form in the market which can be easily adulterated. Detection becomes more difficult as the final product had gone through various incorporations during the manufacturing and production phase. Dyes may be added to make a spice look fresher, older spices may be added to freshly ground ones to increase weight, non-spice material may be added as an extender, or spent spices with valuable constituents removed may be sold as whole spices (Everstine, 2013). The cases related to food fraud in India are significantly increasing according to the Food Safety & Standards Authority of India (FSSAI) enforcement report; 18,550 civil cases and 2,819 criminal cases were reported from 2018- 19 (FSSAI enforcement report, 2021). Food fraud is a growing concern that is affecting the health as well as the economy of society. Fifty seven percent of people developed health problems like stomach disorder, heart problem, anemia, liver disorder, indigestion, nausea, vomiting, diarrhea, dysentery, acidity, ulcer, cancer, kidney malfunction, metabolic dysfunctions, food poisoning, skin disorders, etc, due to consumption of adulterated and contaminated food worldwide (Pal and Mahinder, 2020). Food fraud is estimated to cost the global food industry US $ 10-15 billion per year according to Grocery Manufacturers Association (GMA) (King et al., 2017). Incidents of food fraud are thus found to be detrimental to public health as well as the economy and therefore countermeasures for it need to be developed.

Food forensic is a branch of forensic chemistry that deals with food fraud investigations. Food forensic investigation involves, determining the active constituents, standards and quality assessments, detection of adulterants and contaminants, determination of geographical origin, identifying any safety or quality problems that may be associated with a food product, etc (Mermelstein, 2018). Basically, two main tasks can be done by the application of food forensics; food authentication and food traceability. Food authentication deals with the detection of adulterants and contaminants, quality assessments, and verifications of the labels associated with the food product. Food traceability helps in verifying the origin of the products or deals with finding out the raw materials associated with that food product (Aceto, 2015). To ensure customers' rights and to enforce food law; detection of adulterants and contaminants in foodstuffs is a very important task and forensic analysis can help authorities to gather, examine and interpret pieces of evidence against food fraud.

There are various methods of adulteration and contamination detection, which are physical, chemical, biological, or instrumental methods (Osman et al., 2019; Hong et al., 2017). The instrumental analysis based on the chemical composition of the sample can be divided into two categories– Spectroscopic and Chromatographic analysis.

The chromatographic analysis involves TLC (Jaiswal et al., 2016; Bhooma et al, 2019; Danciu et al., 2018), HPLC (Sebaei and Youssif, 2019), HPTLC (Vadivel et al., 2018), HPTLC-MS (Rani et al., 2015), LC- MS (Bessaire et al., 2019) and GC- MS (Vadivel et al., 2018; Bansal et al., 2015). Chromatographic techniques are the most common techniques applied in food analysis. This is because; chromatography can be applied both to detect adulterations and to determine authenticity (Pastor et al., 2019). GC- MS has been used extensively in food analysis; as food presents a complex matrix and the chromatographic technique can readily and rapidly separate the molecules with extremely similar chemical characteristics even from complex matrices (Lees, 2000). In literature, there are many examples of GC- MS applications being used in food fraud analysis of spices, some recent examples being; establishing organic markers for certain common spices for spice authentication (Atkins, 2015), unknown spices identification and authentication, detection of plant- based adulterants in black pepper (Vadivel et al., 2018; Gul et al., 2017), saffron, fennel and cumin (Xiao-Dong et al., 2015; Farag et al., 2020), confirmatory analysis for electronic screening devices, detection of pesticide residues (Hakme et al, 2018) and also in origin differentiation of cumin & turmeric (Yichen et al., 2014). The motivation for spice fraud is largely attributed to economical interest to gain greater profit margins and such adulteration of spices can have serious implications for public health. Delhi, Uttar Pradesh and Hyderabad police busted a food contamination case of manufacturing fake cumin seeds. The accused reported that they first experimented with making cumin seeds with different types of grass and seeds from the forest. (Gurneel Kaur, 2019). Officers of the enforcement branch of the Kolkata police had on the basis of suspicion seized a large quantity of cumin seeds. The cumin seeds were mixed with sulfa seeds which are very cheap and resemble cumin seeds and is used as cow feed. The Spices Board of India got a huge export consignment of cumin from a Gujarat- based firm seized, after the testing at Kandla Port revealed adulteration and it was reported that there was presence of 23.33 per cent extraneous matter against maximum limit of 3 per cent in the sample which was a clear indication of adulteration (Press Trust of India. business-standard.com, 2018).

Table 1- Samples collected from different markets of Indian cities.

Spice	Sample type	Area of collection	Code
Black pepper (whole)	Local, opened	Local market, South Delhi	PD
		Local market, Meerut	PM
	Branded, closed	Grocery store, South Delhi	PB
Cumin (whole)	Local, opened	Local market, South Delhi	JD
		Local market, Meerut	JM
	Branded, closed	Grocery store, South Delhi	JB
Fennel (whole)	Local, opened	Local market, South Delhi	SD
		Local market, Meerut	SM
	Branded, closed	Grocery store, South Delhi	SB
Coriander (powder)	Local, opened	Local market, South Delhi	CD
		Local market, Meerut	CM
	Branded, closed	Grocery store, South Delhi	CB
Turmeric (powder)	Local, opened	Local market, South Delhi	TD
		Local market, Meerut	TM
	Branded, closed	Grocery store, South Delhi	TB

Spices and herbs, being high-priced commodities, have been often subjected to adulteration in many ways which reduces their quality and potentially has harmful health implications. Adulteration is attributed primarily to increased demand or supply shortage of the spices.

The objective of the present study was to authenticate some household spices- black pepper, cumin, fennel, coriander & turmeric by identifying various active constituents and detecting any adulterant or contaminants in these local samples using the GC- MS technique. The chemical constituents of all the spices were compared with the chemical profile cited in the literature. This study may be helpful for the spice industry to detect the adulteration where physical and other chemical analysis have their own limitations.

Table 2- Volatile compounds detected in black pepper, hexane and ethanol extracts (PD-H, PD-E, PM-H, PM-E, PB-H & PB-E) by GC-MS analysis.

Compounds	PD-H	PD-E	PM-H	PM-E	PB-H	PB-E
3- Carene	✓	✓	✓	✓	✓	✓
4- Carene			✓			
7- epi- cis- Sesquisabinene hydrate		✓				✓
12- Methyl- E, E- 2, 13- octadecadien-1- ol		✓				✓
alpha- Pinene		✓		✓		✓
alpha- Sabinene	✓	✓			✓	✓
alpha- Terpinene			✓		✓	
Aromandendrene			✓		✓	
Azulene	✓					
beta- acorenol				✓		✓
beta- Pinene			✓		✓	
beta- Thujene			✓		✓	
beta- Selinene					✓	✓
Benzoic acid	✓				✓	
Caryophyllene	✓	✓	✓	✓	✓	✓
Caryophyllene oxide	✓		✓			✓
Cedrene						✓
cis- Verbenol, trimethylacetate			✓		✓	
cis- Z- alpha- Bisabolene epoxide			✓			✓
Copaene	✓	✓	✓	✓	✓	✓
D- Limonene	✓	✓	✓	✓	✓	✓
delta- Cadinol	✓	✓	✓	✓	✓	✓
delta- Elemene	✓	✓	✓	✓	✓	✓
Epicubebol		✓		✓		✓
gamma-Muurolene				✓		✓
Ingenol			✓			
Oleic acid	✓	✓	✓	✓	✓	✓
p- Menth- 8- en- 1- ol		✓				✓
p- Mentha- 1(7) ,8- diene						✓
Pellitorine			✓		✓	
Piperanine				✓		
Pipercitine				✓		
Piperidine		✓				✓
Piperine		✓		✓		✓
sia- Limonene				✓		✓
Tau- cadinol acetate		✓		✓		✓
trans- Z- alpha- Bisabolene epoxide				✓		✓

Materials and methods

Spices used

Spices used in the present study were black pepper, cumin, fennel, coriander and turmeric. Samples were collected from local markets of Indian cities of Delhi and Uttar Pradesh. Total of 15 spice samples were purchased from local markets; five of which were branded samples sold in closed packets and the rest 10 were sold in loose open condition. For simplicity, the samples were coded according to Table 1.

Chemicals

Ethyl alcohol and Hexane of AR grade were procured from Hayman Exports Private Limited and SD Fine Chemical Limited, India respectively and were required for solvent extraction. Ethanol was used to extract hydrophilic and polar components while hexane was used to extract hydrophobic and non-polar components of the spices.

Glassware

The glass wares used were Glass vacutainer (15 ml), beaker (50 ml) and GC- MS glass vials (1.5 ml); which were procured from Borosil, India.

Sample preparation

One gram of each spice in ground form (the whole forms were roughly grinded using mortar & pestle) was taken into a glass vacutainer (15 ml). To this 15 ml solvent (ethanol/ hexane) was added and was covered tightly with a cork. The labeled vacutainers were than kept in a cold storage for one week, at 4 degree Centigrade. The supernatant was than collected in the GC-MS glass vials (1.5 ml). The extracts prepared were PD- H, PD- E, JD- H, JD- E, SD- H, SD-E, CD- H, CD- E, TD- H, TD- E, PM- H, PM-E, JM- H, JM- E, SM- H, SM- E, CM- H, CM-E, TM- H, TM- E, PB- H, PB- E, JB- H, JB- E, SB- H, SB- E, CB- H, CB- E, TB- H, & TB-E (H= hexane & E= ethanol).

Table 3- Volatile compounds detected in cumin, hexane and ethanol extracts (JD-H, JD-E, JM-H & JM-E, JB-H & JB-E) by GC-MS analysis.

Compounds	JD-H	JD-E	JM-H	JM-E	JB-H	JB-E
1, 3- p- Methadien- 7- al	✓		✓		✓	
1, 3, 8- p- Methatriene		✓				
1, 4- p- Methadien- 7- al		✓		✓		✓
2- decalinyl acetate				✓		✓
2, 5- octadecadiytioic acid				✓		✓
3- Caren- 10- al			✓			
3- p- Menthen- 7- al	✓		✓		✓	✓
4- (3, 3- dimethylbut- 1- ynyl)- 4- hydroxy- 2, 6, 6- trimethylcyclohex- 2- enone	✓		✓		✓	
beta- Caryophyllene	✓	✓			✓	✓
beta- Cymene			✓	✓	✓	✓
beta- Ionene						✓
beta- Pinene	✓	✓	✓	✓	✓	✓
Carotol	✓	✓	✓		✓	✓
Caryophylla- 4(12), 8(13)- dien- 5- beta- ol		✓		✓		✓
cis- Carveol		✓		✓		✓
Cuminaldehyde	✓	✓	✓	✓	✓	✓
Epicubebol				✓		✓
gamma- Muurolene	✓				✓	
gamma- Terpinene	✓	✓	✓	✓	✓	✓
o- Cymene	✓				✓	
Propanoic acid		✓				✓
Sabinene hydrate			✓		✓	
sia- Cumene					✓	

Instrumental parameters

GC- MS analysis was performed on an Agilent 7890B GC system having 7693 auto-sampler unit and fitted with 30 m long capillary column having 0.25 mm inner diameter and film thickness of 0.25 µm; coupled with Agilent MS- 5977A Mass Selective Detector (MSD). Helium gas is used as carrier gas at flow rate of 3 ml/ min and nitrogen was used as makeup gas. The oven temperature was programmed from

60 degree centigrade to 170 degree centigrade at 40 degree centigrade/ min and held for 10 min, then raised to 300℃ at 10 degree centigrade/ min and held for 5 min and finally the maximum temperature was 310 degree centigrade. It was operated on splitless mode. The injector, MS source & MS quad temperature were 60℃, 230℃ and 150℃ respectively. The injection volume was 1 µL. MS were taken at 70 eV with a mass scan range of m/z 40- 550. The compounds were then identified using NIST library database.

Result and discussion

Identification of active constituents of spices

From the GC- MS analysis of the spice samples, various active constituents were detected qualitatively. The results were represented in Tables 2- 6. The findings clearly shows that Black pepper contains piperine, piperidine, pipercitine, beta- carophyllene, 3-carene, alpha- pinene, copaene, delta- elemene, delta- cadinol, muurolene, etc; Cumin contains cuminaldehyde, 1, 3- p- menthadien- 7- al, beta-caryophyllene, pinene, o- cymene, beta-cymene, alpha- terpinene, gamma- terpinene, carotol, cis- carveol, etc; Fennel contains anethole, estragole, fenchone, d- limonene, p-acetonylanisole, etc; Coriander contains linalool, geranyl vinyl ether, nerolidol, oleic acid, lactic acid, leucine, nerolidyl acetate etc and Turmeric contains alpha- curcumene, beta-curcumene, turmerone, turmerol, curlone, atlantone, zingiberene, tumerone, nuciferol, zizanol, etc. Major flavor compounds, according to the spice board of India detected in the spices by the GC- MS analysis were Piperine, Carophyllene & 3- Carene in black pepper; Cuminaldehyde and 1, 3- methadien- 7-al in cumin; Anethole and Fenchone in fennel; Linalool and Geranyl vinyl ether in coriander and Turmerone and Zingeberene in turmeric.

Table 4- Volatile compounds detected in fennel, hexane and ethanol extracts (SD-H, SD-E, SM-H, SM-E, SB-H & SB-E) by GC-MS analysis.

Compounds	SD-H	SD-E	SM-H	SM-E	SB-H	SB-E
1- chloro- decane			✓		✓	
1- chloro- dodecane			✓		✓	
1, 2- Benzenedicarboxylic acid				✓		✓
2- bromo- octadecanal			✓		✓	✓
2- Tetradecanol				✓		✓
2, 3- dimethyl- 55- trifluoromethyl- phen- 1, 4- diol		✓				✓
3- chloro- 2- butanol		✓		✓		✓
3- Eicosanone	✓				✓	
(3E, 5E)- 2, 6- dimethylocta- 3, 5, 7- trien-2- ol		✓		✓		✓
3- ethyl-5-(2- ethylbutyl)- octadecane			✓		✓	
Anethole	✓	✓	✓	✓	✓	✓
beta -Terpineol				✓		✓
cis- Vaccenic acid			✓	✓	✓	✓
cis- Verbenol			✓		✓	
D- Limonene	✓	✓	✓		✓	✓
Estragole	✓	✓	✓	✓	✓	✓
Fenchone	✓	✓	✓	✓	✓	✓
Hexadecanoic acid						✓
Leucine		✓				
Linalyl acetate				✓		✓
Mesitylene			✓			
Nonacosan- 10- one	✓		✓			✓
Oleic acid		✓				✓
p- Acetonylanisole	✓				✓	
p- Menthan- 2- ol	✓					
p- Menth- 8- en- 1- ol		✓				✓
Phthalic acid						✓

Table 5- Volatile compounds detected in coriander, hexane and ethanol extracts (CD-H, CD-E, CM-H, CM-E, CB-H & CB-E) by GC-MS analysis.

Compounds	CD-H	CD-E	CM-H	CM-E	CB-H	CB-E
1-chloro-dodecane			✓		✓	
2-(1-cyclohexenyl)-clyclohexanone		✓				✓
2,4-Dimethylhexane	✓				✓	
2,5-Dihydrobenzoic acid					✓	
2-bromo-octadecanal	✓				✓	
2-Myristynoyl pantheine		✓				✓
9,12-Octadecadienoic acid (Z,Z)-				✓		✓
Acetoin		✓				
cis-7-Hexadecenoic acid				✓		✓
cis-10-Octadecenoic acid		✓			✓	✓
cis-13-Octadecenoic acid	✓				✓	✓
cis-Vaccenic acid				✓		✓
cis-Verbenol, trimethylacetate			✓		✓	
Enol						✓
Ethyl oleate		✓				✓
Geranyl vinyl ether		✓				✓
L-Lactic acid		✓				✓
L-Lucine			✓			
Linalool	✓	✓		✓	✓	✓
Nerolidol	✓				✓	
Nerolidyl acetate			✓		✓	
n-Hexadecanoic acid	✓	✓			✓	✓
Octadecyl vinyl ether						✓
Oleic acid	✓	✓		✓	✓	✓
Phorbol		✓				✓
Pterin-6-carboxylic acid				✓		✓

The following depictions (Fig. 1) show the TIC (total ion chromatogram) scan and MS (mass spectrum) Spectrum for the flavor compounds detected. The chemical profile generated for each spice extract is valuable in their identification and authentication. The samples which were considered authentic on the basis of this analysis were SM and CM.

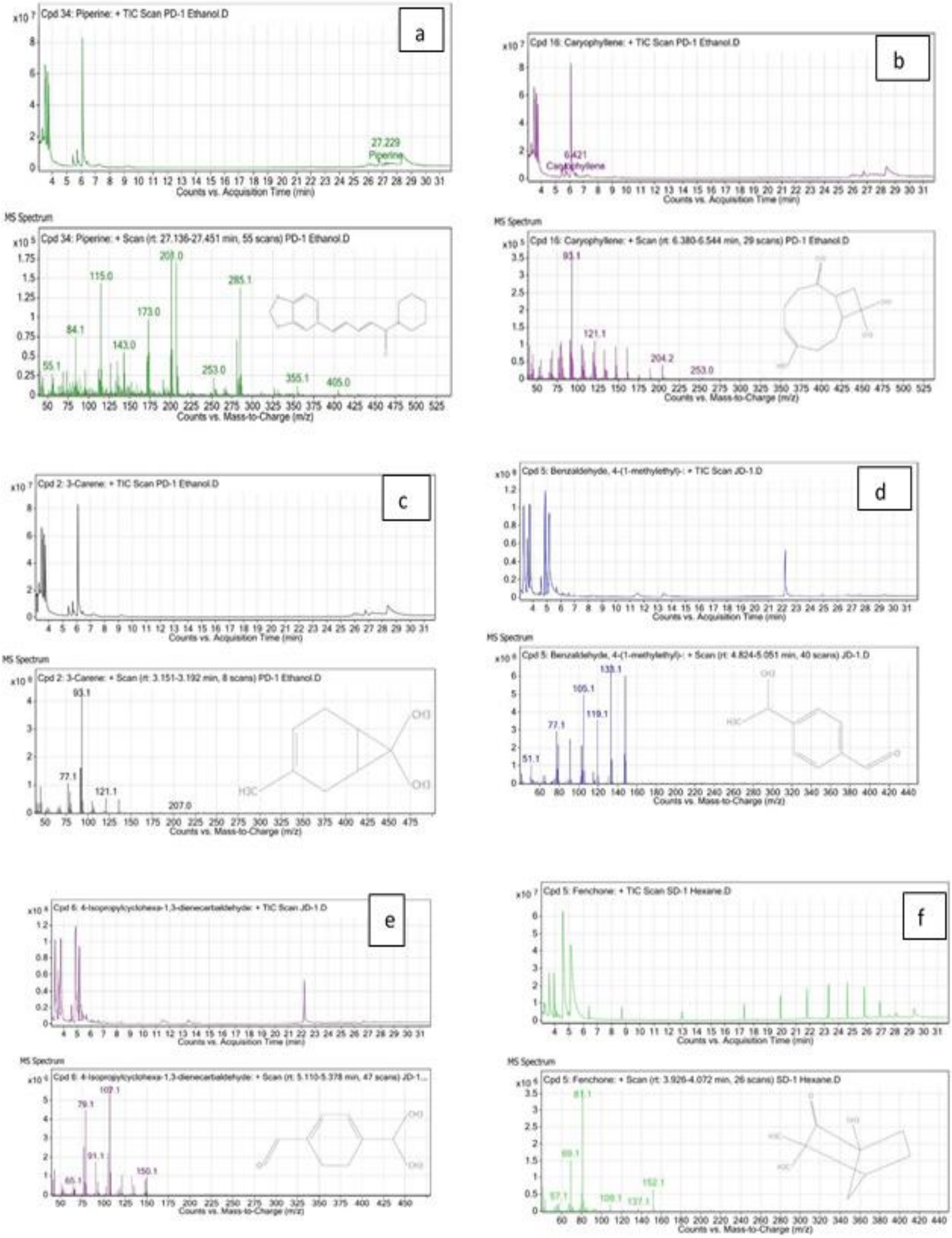
Detection of adulterants and contaminants

Table 7 describes the qualitative detection of adulterants and contaminants in the samples. All the foreign materials detected in the analysis can be classified into adulterants, contaminants, agricultural contaminants, manufacturing contaminants, and industrial waste. The spices were collected randomly for conducting food forensic investigation, to detect any fraud. A total of 15 samples were analyzed. The samples analyzed as adulterated or contaminated products were PD, JD, CD, TD, SD, PM, JM, and TM. According to the analysis, out of 10 local samples 4 of them were found to be adulterated. In sample JD, the admixture of black cumin was observed; in TD, the admixture of wild turmeric was observed, in PM, the admixture of papaya seeds was observed and in JM, the admixture of aniseed was observed. All the adulterants detected in the study were plant- based, which is difficult to be detected by traditional analysis which involves physical and chemical tests. PD, SD, CD & TM were found to be contaminated by manufacturing, industrial and agrochemical contaminants. PD was contaminated by algae, *Sargassium vulgare*, which might be incorporated from contaminated water; SD was found to be contaminated by agrochemicals, ethylene oxide and carbanilide and also contain plastic waste, dibutyl phthalate; the CD was contaminated with agrochemicals, ethylene oxide and carbanilide, it was also infected by a soil fungus, *Pennicilum expansum* and also contain plastic waste, dibutyl phthalate, and beta- curcumene, ar- turmerone and curlone was present as manufacturing cross contaminant; TD was contaminated with a fumigating agent, ethylene oxide and TM was infected by a soil fungus, *Pennicilum expansum* and also found to contain plastic waste. They were also contaminated as a result of agricultural cross- contamination which is non-intentional and might be present due to the cultivation proximity or during distribution and storage of these products. Study on the types of adulterants added in the spices powder according to consumer's suspect has revealed that addition of low-grade raw spice with high grade was at the top position (Sattar et al., 2019).

Table 6- Volatile compounds detected in turmeric, hexane and ethanol extracts (TD-H, TD-E, TM-H, TM-E, TB-H & TB-E) by GC-MS analysis.

Compounds	TD-H	TD-E	TM-H	TM-E	TB-H	TB-E
1- (3- cyclopentylpropyl)- 2, 4- benzene	✓				✓	
1- Heptatriacotanol		✓				✓
3- Carene				✓		✓
4- Carene				✓		✓
4- epi- alpha- acoradiene	✓					
5`methyl- 2`hydroxy- acetophenone		✓				✓
6S, 7R- Bisabolone			✓		✓	
alpha- Curcumene	✓	✓	✓	✓	✓	✓
aR- Turmerol	✓	✓	✓	✓	✓	✓
aR- Turmerone	✓	✓	✓	✓	✓	✓
beta- Curcumen- 12- ol	✓	✓		✓	✓	✓
beta- Curcumene		✓	✓	✓	✓	✓
beta- Pinene				✓		✓
beta- Sesuiphellandrene	✓	✓	✓	✓		
beta- Turmerone	✓				✓	
Bisabolone				✓		✓
Caryophyllene			✓			
cis- Verbenol, trimethylacetate			✓		✓	
Curlone	✓	✓	✓	✓	✓	✓
Cyclohexene epoxide	✓	✓	✓		✓	✓
(E)- Atlantone	✓	✓	✓	✓	✓	✓
Eudesmol				✓		✓
Hexylene glycol					✓	
Humulenol- II			✓	✓	✓	✓
n- Hexadecanoic acid			✓	✓	✓	✓
Nuciferol		✓	✓	✓	✓	✓
Oleic acid			✓	✓	✓	✓
trans- Sesquisabinene hydrate		✓	✓			
trans- Z- alpha- Bisabolene epoxide			✓		✓	
Tumerone		✓	✓	✓	✓	✓
(Z)- gamma- Atlantone		✓	✓	✓	✓	✓
Zingiberene		✓	✓	✓	✓	✓
Zizanol		✓		✓		✓

Detection of food fraud is an enormous challenge because consumers cannot detect them and those involved in the fraud business embrace innovative ways to avoid detection. New challenges with regard to addressing food fraud are related to astronomical growth of e-commerce of food. Two connected avenues for preventing and controlling food fraud are legal interventions and technological innovations. TLC method to detect the adulteration of black pepper powder with ground papaya seed has been reported (Paradkar et al., 2001). Detection of trans- anethole in the essential oil composition of cumin seeds has been reported as an indication towards the presence of contamination with low grade fennel seeds in which trans- anethole is a major marker compound (Dinesh Singh Bisht et al., 2014).



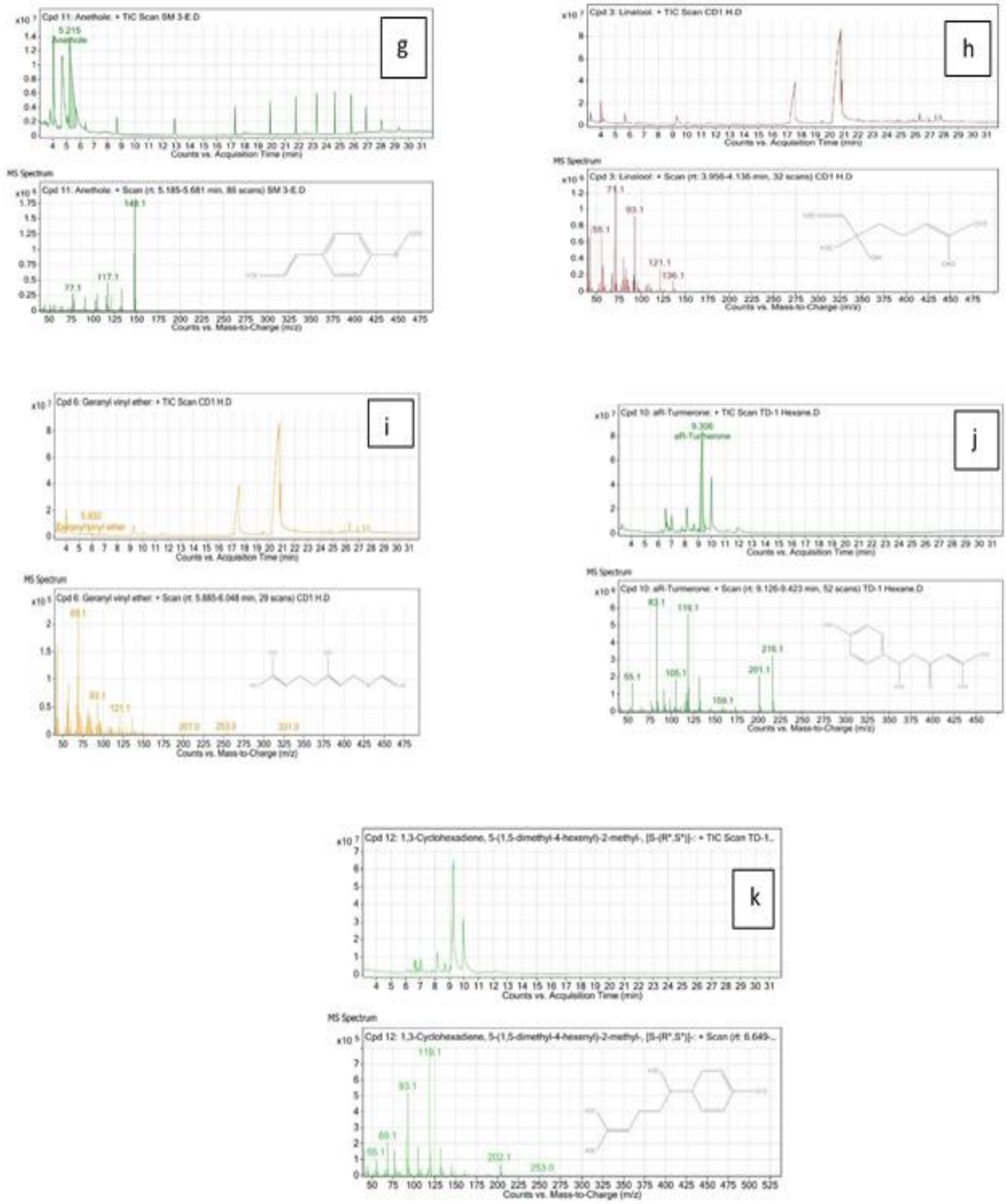


Fig. 1. Flavor compounds detected in the analysis.

TIC scan and MS spectrum of (a) Piperine, (b) Caryophyllene, (c) 3-Carene detected in *Piper nigrum* (black pepper); (d) Cuminaldehyde, (e) 1,3-p-menthadien-7-al detected in *Cuminum cyminum* (cumin); (f) Fenchone (g) Anethole detected in *Foeniculum vulgare* (fennel); (h) Linalool (i) Geranyl vinyl ether detected in *Coriandrum sativum* (coriander) and; (j) Turmerone, (k) Zingiberene detected in *Curcuma longa* (turmeric).

Table 7- Adulterants or contaminants detected in spice samples (*Abbreviations used are: "A" – Adulterant; "C" – Contaminant (including microbial infection and agrochemical residues); "G" – Agricultural cross contaminant; "M" – Manufacturing contaminant; "I" – Industrial waste.)

Compound	Type	Sample	Inference	Ref.
Valencene	G	PD-H PD-E	It is a metabolite of plant, *Piper betle (*Betle vine*)*. The sample might have been contaminated with this while agricultural practice.	Barata et al. (2021)
Dihydro- 3- isooctadecyl- 2, 5- Furandione	C	PD-H	It is a bioactive product of an alga, *Sargassium vulgare*. This was present as a contaminant, from contaminated water bodies.	Shreadah et al. (2018)
Limonen- 6- ol pivalate	A	JD-H	It is a bioactive product of *Nigella sativa* (Black cumin); it was present as an adulterant.	Hadi et al. (2016)
alpha- Longipinene	A	JD-H	It is a volatile of *Nigella sativa* (Black cumin); it was present as an adulterant.	Kabir et al. (2020)
Brassicasterol	G	JD-H	It is a product of rapeseed's EO; it was present as an agricultural cross contaminant.	Gul and Seker, (2006)
Ethylene oxide	C	SD-H CD-H TD-H	It is used as a fumigating agent, which is toxic in nature and thus banned in practice.	https://www.epa.gov/sites/production/files/2016-09/documents/ethylene-oxide.pdf> (assessed on 10.05.21) https://www.who.int/ipcs/publications/cicad/en/cicad54.pdf>(assessed on 10.05.21)
Carbanilide	C	SD-E CD-E	It was present as a pesticide residue.	https://patents.google.com/patent/EP1443045A9/en> (assessed on 10.05.21)
Dibutyl phthalate	I	SD-E CD-E	It is used as plasticizer, which might be present due to poor packaging material.	https://cameochemicals.noaa.gov/chemical/5717> (assessed on 10.05.21)
Lavandulol	G	CD-H	It is an active constituent of lavender's EO and was present as an agricultural cross contaminant.	https://pubchem.ncbi.nlm.nih.gov/compound/4-Hexen-1-ol_-5-methyl-2-_1-methylethenyl> (assessed on 10.05.21)
beta- Curcumen- 12- ol	M	CD-H	It is an active compound of turmeric which might be present as a manufacturing cross contaminant.	[Table 6]
ar- Turmerone	M	CD-H CD-E	It is an active compound of turmeric which might be present as a manufacturing cross contaminant.	[Table 6]
Curlone	M	CD-H CD-E	It is an active compound of turmeric which might be present as a manufacturing cross contaminant. This might be because of using unclean industrial instrument during manufacturing.	[Table 6]
2- amino- 5- [(2- carboxyl)vinyl] – Imidazole	C	CD-E TM-E	It is a metabolite which belongs to fungus, *Pennicillum expansum*. It was present as a fungal contaminant.	Hamza et al. (2015)

Formic acid, 3, 7, 11- timethyl- 1, 6, 10- dodecatrien- 3- yl ester	G	CD-E	It is an active compound of *Citrus limonum* (lemon); it was present as an agricultural cross contaminant.	Ainane et al. (2018)
1H- 3a, 7- Methanoazulene	A	TD-H	It is a constituent of *Curcuma aromatica*, which is a wild turmeric species and it was a plant based adulterant which compromises the quality of product.	Umar et al. (2020)
7- (1, 3- dimethylbuta-1, 3- dienyl) -1, 6, 6- trimethyl- 3, 8 – dioxatricyclo [5.1.0.0(2,4)] octane	G	TD-E	It is a phytoconstituent of agarwood which is present in the sample as an agricultural contaminant.	Peng et al. (2020)
Linoleic acid	A	PM-H	It is a phytoconstituent present in papaya seeds. It is the most common adulterant used in black peppercorns.	https://phytochem.nal.usda.gov/phytochem/plants/show/346?qlookup=papaya&offset=0&max=20&et=> (assessed on 17.05.21)
2- bromo- octadecane	A	PM-H PM-E	It is a phytoconstituent present in papaya seeds. It is the most common adulterant used in black peppercorns.	https://phytochem.nal.usda.gov/phytochem/plants/show/346?qlookup=papaya&offset=0&max=20&et=> (assessed on 17.05.21)
Tricosenoic acid	A	PM-H PM-E	It is a phytoconstituent present in papaya seeds. It is the most common adulterant used in black peppercorns.	https://phytochem.nal.usda.gov/phytochem/plants/show/346?qlookup=papaya&offset=0&max=20&et=> (assessed on 17.05.21)
1, 4, 7- Cycloundecatriene, 1, 5, 9, 9- tetramethy- Z, Z, Z-	G	PM-H	It is a phytochemical of *Piper longum*; which is present in sample as an agricultural cross contaminant.	https://assets.researchsquare.com/files/rs-31834/v1/SupplementaryTableS1.docx> (assessed on 17.05.21)
Myristic acid	A	PM-E	It is a phytoconstituent present in papaya seeds. It is the most common adulterant used in black peppercorns.	https://phytochem.nal.usda.gov/phytochem/plants/show/346?qlookup=papaya&offset=0&max=20&et=> (assessed on 17.05.21)
Phthalic acid, butyl hex- 3- yl ester	A	PM-E	It is a phytoconstituent present in papaya seeds. It is the most common adulterant used in black peppercorns.	https://phytochem.nal.usda.gov/phytochem/plants/show/346?qlookup=papaya&offset=0&max=20&et=> (assessed on 17.05.21)
12- hydroxyoctadecanethioic acid, S- t- butyl ester	G	PM-E	*Radermachera xylocarpa*, present as an agricultural contaminant.	Ekade & Manik, (2014)
Artemisia alcohol	A	JM-H	It is an active constituent of aniseed (sweet cumin); which was used as an adulterant in this cumin sample.	Koul et al. (2017)

Thujyl acetate	A	JM-H	It is an active constituent of aniseed (sweet cumin); which was used as an adulterant in this cumin sample.	https://phytochem.nal.usda.gov/phytochem/plants/show/1502?qlookup=Pimpinella+anisum&offset=0&max=20&et=> (assessed on 17.05.21)
Linalool hydroxyl	A	JM-H	It is an active constituent of aniseed (sweet cumin); which was used as an adulterant in this cumin sample.	https://phytochem.nal.usda.gov/phytochem/plants/show/1502?qlookup=Pimpinella+anisum&offset=0&max=20&et=> (assessed on 17.05.21)
gamma-Cadinene	A	JM-H	It is an active constituent of aniseed (sweet cumin); which was used as an adulterant in this cumin sample.	https://phytochem.nal.usda.gov/phytochem/plants/show/1502?qlookup=Pimpinella+anisum&offset=0&max=20&et=> (assessed on 17.05.21)
cis-beta-Farnesene	A	JM-H	It is an active constituent of aniseed (sweet cumin); which was used as an adulterant in this cumin sample.	https://phytochem.nal.usda.gov/phytochem/plants/show/1502?qlookup=Pimpinella+anisum&offset=0&max=20&et=> (assessed on 17.05.21)
cis- Thujapsene	A	JM-H	It is an active constituent of aniseed (sweet cumin); which was used as an adulterant in this cumin sample.	https://phytochem.nal.usda.gov/phytochem/plants/show/1502?qlookup=Pimpinella+anisum&offset=0&max=20&et=> (assessed on 17.05.21)
Bisabolene	A	JM-H	It is an active constituent of aniseed (sweet cumin); which was used as an adulterant in this cumin sample.	https://phytochem.nal.usda.gov/phytochem/plants/show/1502?qlookup=Pimpinella+anisum&offset=0&max=20&et=> (assessed on 17.05.21)
alpha- Selinene	A	JM-H	It is an active constituent of aniseed (sweet cumin); which was used as an adulterant in this cumin sample.	https://phytochem.nal.usda.gov/phytochem/plants/show/1502?qlookup=Pimpinella+anisum&offset=0&max=20&et=> (assessed on 17.05.21)
Fumaric acid, 3-phenylpropyl-tridec- 2- yn- 1- yl ester	I	TM-H TM-E	It is a plastic waste which might have incorporated in the product due to poor packaging material.	Chiwara et al. (2018)
Cyclohexene, 4-isopropenyl- 1 – methoxymethoxy - methyl-	G	TM-E	It is present as an agricultural contaminant; it belongs to Artemisia annua.	Hameed et al. (2016)

Bicyclo [4.4.0]dec- 2- ene- 4- ol, 2- methyl- 9- (prop- 1- en- 3-ol- 2- yl)-	G	TM-E	It is a constituent of Ginger; which is present as a result of agricultural cross contamination.	Shareef et al. (2016)
Estra- 1, 3, 5 (10)- trien- 17- beta-ol	G	TM-E	It is a constituent of Ginger; which is present as a result of agricultural cross contamination.	Shareef et al. (2016)

Since quality control and safety monitoring has become a pressing issue for the spice industry. DNA barcoding in combination with morphological sorting and DNA metabarcoding, a combinatory approach of microscopy, chemical analysis and classical DNA barcoding of the isolated contaminants using the *matK* and *trnHpsbA* loci has been reported to provide qualitative and quantitative information on the amount of plant material responsible for the contaminations and the extent of the contamination (Willocx et al., 2014).

Literature survey reveals that the quality of spice is lost due to the presence of contaminants, filth matter, mycotoxins and heavy metals. Techniques like IRMS, NMR, FT- IR acts as a fingerprinting tool to effectively detect adulteration of spices and spice products even at trace levels (Bharathi et al., 2018). However, the major drawbacks in these technologies are their establishment and running cost. Thus the robustness of GC- MS as an analytical technique in detecting adulterants discussed in this paper is of significance in the forensic examination of seizures of spices. The adulterations identified in this study were economically motivated and the admixture of such cheaper and similar- looking plant materials does compromise the quality of the spices.

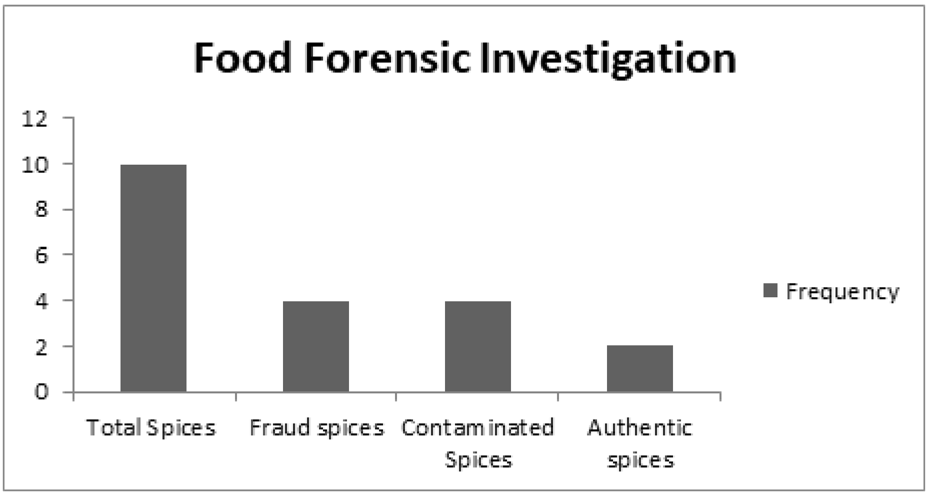


Fig. 2. Food forensic investigation; Bar graph showing the numbers of spices found to be adulterated, contaminated and those which were safe from any adulterants and contaminants.
Only the local products are taken into the consideration as branded samples were only used for reference.

The fraud detected in this investigation was adulteration; where adulterants that look similar to authentic spices were sold in the local markets. The algal or fungal contamination observed in PD, CD and TM is due to contamination of the environment surrounding cultivation, irrigation, distribution, or storage. Hygiene must be maintained in the food industry, it is important for the production of safe and high- quality products. The plastic waste or product of plasticizer detected in the GC- MS analysis represent the poor choice of packaging which is done in local market and needs to be upgraded with much better biodegradable option. The agrochemicals detected in the sample were carbanilide and ethylene oxide; both are unsafe for human consumption. The food forensic investigation conducted can be summarized in the following chart (Fig. 2).

Differentiation of samples based on their source

Many phytoconstituents were detected through the GC- MS analysis of the spices. The spices were collected from two different regions Delhi and Uttar Pradesh in India. The differences between them can be established by the help of the chemical profiles of the spices. PD contains piperine and piperidine while PM contains piperine, pipercitine and piperanine. JD contains o- cymene and gamma- muurolene while JM contains beta- cymene and 3- caren-10- al. SD contains p- menthan- 2- ol, p-acetonylanisole and p- menth- 8- en- 1- ol while SM contains mesitylene and beta- terpineol. CD contains geranyl vinyl ether while CM contains nerolidyl acetate. TD contains beta- turmerone and TM contains beta- pinene and caryophyllene. Further comparisons of both the varieties, on the basis of number of active constituents detected and number of foreign compounds detected in the samples are represented in Fig. 3.

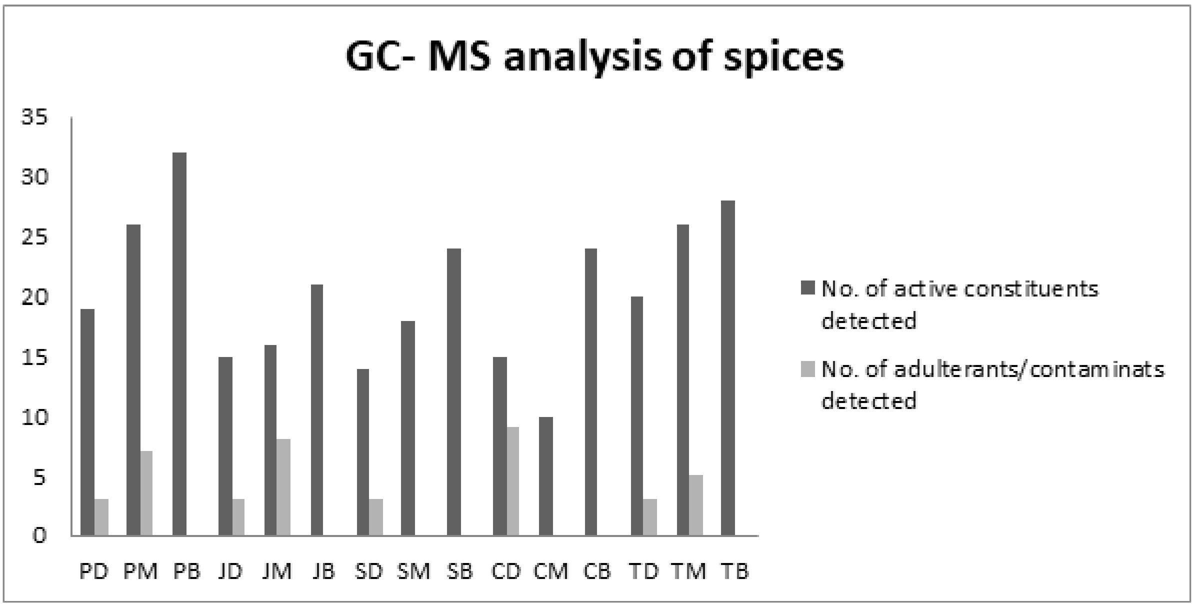


Fig. 3. Bar-graph showing the comparison done between the different samples.

The GC- MS qualitative analysis of spices results in formation of a chemical profile which can be used in identifying authentic products. Also it assists in detection of plant-based adulterants, agrochemicals, microbial infections and even plasticizers used in packaging. The instrument is very sensitive and can detect compounds in minute concentration and thus able to identify both primary and secondary metabolites of the spice samples. The chemical profile is useful for identification as well as differentiation of samples from different source. The volatiles of spice's extracts were readily analyzed using the GC-MS analysis and thus it proves to be an effective analytical tool in food analysis.

Conclusion

Spice adulteration is a highly dynamic fraudulent practice. Economically motivated adulteration is found in a wide variety of spices and adulteration is now a global challenge and at risk are spices and herbs as exemplified by the simple adulteration of cumin with anise seeds. Despite having a regulatory body the food fraud instances are rising globally and especially during the pandemic covid- 19 there have been numerous instances of panic buying, buying from e- commerce websites which diluted the quality requirements and checks of spices used in the present study i.e. black pepper, cumin, fennel, coriander and turmeric. The food fraud investigations conducted by the food authorities are mostly targeted analyses. Therefore non- targeted analysis may prove to be more effective in food fraud detection. Analytical techniques like visual/ sensorial evaluations of plant material with microscopy, chromatographic and spectroscopic methods have been reported there to detect the adulteration of spices and herbs. Food forensic investigation conducted on the spices using GC- MS technique proved to be effective in detecting adulterants as well as contaminants and the qualitative results may be an important reference for law authorities to prevent and control food quality and health safety issues involved therein. The GC- MS qualitative analysis helps to authenticate the spices and the chemical profile generated can be a reference tool in further differentiation based on the sources and quality of the product. DNA- based techniques have now emerged as authentication tool for discrimination between closely related species and cultivars. Essential oil compositions of spices may be a future tool for predicting adulteration/ contamination and further studies on standardization and validation of active ingredients using various instrumentation techniques like GC- MS, HPTLC- MS, LC- MS can be undertaken for food fraud investigation.

Acknowledgement

The authors express their sincere gratitude to Mrs. Deepa Verma, Director, Forensic Science laboratory, NCT of Delhi, Shri K.C. Varshney, Head of office, Regional Forensic Science Laboratory, Chanakyapuri, New Delhi for their keen interest and encouragement. Research experience for postgraduate participant was supported by Department of Anthropology, University of Delhi.

Contribution of authors

Dr.Kanak Lata Verma: Conceptualizing, designing, supervising and interpreting the data pertaining to this research article.

Dr. Pallavi Choudhary: literature review, instrumental analysis, data analysis and participated in drafting the manuscript.

ArpitaSethi: literature review, data analysis and participated in drafting the manuscript.

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Iranian Food Science and Technology Research Journal
Vol. 18, No. 3, Aug. Sep. 2022, p. 31-51

نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد ۱۸، شماره ۳، مرداد - شهریور ۱۴۰۱، ص. ۵۱-۳۱

شناسایی مواد تقلبی و آلاینده‌ها در فلفل سیاه، زیره، رازیانه، گشنیز و زردچوبه با استفاده از تکنیک GC-MS برای تحقیقات پزشکی قانونی

P. Choudhary[1], A. Seth[2], K. Lata Verma[3*]

تاریخ دریافت: ۱۴۰۰/۱۲/۱۲
تاریخ پذیرش: ۱۴۰۱/۰۱/۲۹

چکیده

تحقیقات پزشکی قانونی برای شناسایی مسائل کیفیت و ایمنی مرتبط با غذا و محصول آن بسیار حیاتی است. از GC-MS به‌طور گسترده در تجزیه و تحلیل مواد غذایی استفاده می‌شود. مطالعه حاضر، برای شناسایی ترکیبات فعال برخی از ادویه‌های خانگی و همچنین برای شناسایی مواد تقلبی و آلاینده‌هایی که ممکن است در نمونه‌ها وجود داشته باشد، استفاده شده است. ادویه‌های مورد استفاده در تحقیق حاضر فلفل سیاه، زیره، رازیانه، گشنیز و زردچوبه می‌باشد. عصاره ادویه‌ها با شناسایی ترکیبات فعال مختلف ادویه‌ها، مانند پیپرین، کاریوفیلن و ۳-کارن در فلفل سیاه، کومینالدئید و ۱، ۳- متادین- ۷- آل در زیره سبز، آنتول و فنچون در رازیانه، لینالول و ژرانیل وینیل اتر در گشنیز و تورمرون و زینجی برن در زردچوبه در احراز هویت این ادویه‌ها مفید بودند. مواد تقلبی شناسایی‌شده از نظر کیفی، تقلبی‌های گیاهی بودند. ثابت شده است که GC-MS یک ابزار موثر در تشخیص مواد تقلبی گیاهی، آلاینده‌های میکروبی، و پسماندهای شیمیایی کشاورزی و همچنین زباله‌های صنعتی و تولیدی است.

واژه‌های کلیدی: GC-MS، تقلب ادویه، احراز هویت ادویه، آلاینده‌های ادویه، کیفی.

۱و ۳- آزمایشگاه منطقه‌ای علوم پزشکی قانونی، دولت NCT دهلی، وزارت خانه، Chanakyapuri، دهلی نو، ۱۱۰۰۲۱، هند.
۲- گروه انسان شناسی، دانشگاه دهلی، دهلی، ۱۱۰۰۰۷، هند.