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## Application of mass spectrometry in detection of food adulteration: A review

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### Abstract

Food adulteration detection is the key to food quality and it can be helped by modern analytical techniques. Mass spectrometry is very powerful analytical and it is particularly so when it is combined with other separation techniques like liquid or gas chromatograph because of combination of separation and detection powers. Present review focus on application of mass spectrometry in adulteration detection in food products. It was found at the end of review that almost any conceivable adulteration can be detected by mass spectrometry when used as detection method along with chromatographic separation techniques and mass spectrometry alone without any pre separation techniques is also capable of adulteration detection.

**Keywords:** Adulteration detection, mass spectrometry, review

### Introduction

#### History

Anode rays was discovered in 1886 and after that in 1898 Wilhelm Wien demonstrated that anode rays can be deflected using strong electric and magnetic fields. MS as a technique was invented by J. J. Thomson in 1913 to study isotopes i.e. he done actual measurement of mass to charge ratio using method. His student F. W. Aston advanced Thompson's work reporting dedicated MS machine in 1919.

#### Working Principle

Mass spectrometry is technique for analysis of mass to charge ratio. Mass spectrometer works on ions in gaseous form so everything which can be converted to ions in gaseous form can be analyzed by this technique. There are various techniques for ionization of sample. The ionized sample is passed through magnetic field and ions are separated by mass to charge ratio. Various mechanisms are applied for ion separation by magnetic field or electric field and the part of instrument responsible for this is called mass analyzer. The ions hit the detector and you get signal. Again there are number of detectors.

#### Variations

Basic technique remains same but lot of ions sources, ions selectors and detectors give rise to lot of machine configurations. Some of the machine configurations have special names and they are so different that they are considered separate sub-techniques. Mass spectrometer work under vacuum and thus most of ion sources are also work under vacuum but there are exceptions to this.

#### Common Ion Sources

Multi-photon ionization, electron ionization, chemical ionization, atmospheric chemical ionization, inductively coupled plasma ionization, electron cyclotron resonance ionization, glow discharge ionization, plasma afterglow ionization, spark ionization, particle bombardment ionization, laser desorption ionization and variations like MALDI, electro spray ionization, thermal ionization, ambient ionization techniques like DESI, DART, atmospheric solid analysis probe, rapid evaporative ionization etc. are most common.

#### Popular Mass Analyzers

Sector type, time of flight, quadrupole, ion traps like orbitrap, penning trap or cyclotron which doubles as mass analyzer cum detector. Orbitrap will also act as mass analyzer cum detector.

Best mass analyzers are orbitrap > TOF > cyclotron > quadrupole as per their sensitivity, scanning speed and popularity.

### Detectors

There is only one type of detectors which dominate industry and that is detectors based on electron multiplication effect. Micro channel plate detector arrangement is common. Photons can be converted to electrons for detection if one wants to use them.

### Applications

#### General Applications

HPLC MS MS is reference method for melamine adulteration detection in milk. GC MS MS is also used for this purpose. Vegetable oils and fats added to milk fat is also detected using mass spectrometry along with chromatography. It is also used for detection of preservatives and other substances [1]. Various MS based methods are developed to detect melamine in milk and dairy products. Some of the methods are sample preparation free but many use simple extraction as sample preparation [2].

MS-based protein profiling, using either MALDI-TOF or ESI-MS, has been extensively investigated for the possible detection of fraudulent practices in the dairy industry. The use of the MS protein profiling method provides a shorter analysis time due to a faster sample preparation step that skips protein digestion by selective enzyme [3]. Faster sequencing is particularly true for top down approach but even bottom up approaches uses MS with cutting enzyme this day i.e. Edman Degradation is historic relic.

Mass spectrometry is used as sensor in e-nose systems [4]. Oils, wines, honey, spices, milk etc. can be analyzed using such nose for adulteration detection.

Ambient mass spectrometry AMS is used generally with no or little sample preparation. It has been used for adulteration detection in milk, butter, cheese, vegetable oils, fish, meat, drinks, fruits and vegetables etc. Some studies found AMS without chromatographic separation is vulnerable to variations in sample matrix. Qualitative analysis is more successful than quantification of adulteration using AMS but there are many successful studies [5].

Quick pesticide detection in real time can be successfully done in food using ion mobility MS technique i.e. no sample preparation. Veterinary drugs, natural toxins, melamine, synthetic colors, artificial sweeteners, etc. can be detected and measured. Corona discharge and ESI are most popular ionization techniques reported with IM-MS [6].

Liquid chromatography coupled with high resolution mass spectrometry was used for detection and estimation of contaminants and adulterants using non targeted screening approach. Non targeted approach means finding ideal mass spectra for pure food and if anything deviates from that it is adulteration and attempt is done to identify that thing. Due to inherent variation in food it is difficult to develop ideal MS profile but it can be successful if inherent variation is less i.e. identification of particular variety of tomato soup [7].

GC coupled with MS detector was used to detect oil and fat adulteration based on TAG profiles. High temperature required to make TAG volatile limit choice of GC columns. Compared to this LC provide advantages and samples also remain stable due to low temperature. Thus LC MS become more popular for TAG analysis in recent times. APCI is most common ionization technique i.e. less fragmentation and thus

simpler spectra. As each oil give unique fingerprint spectra it is possible to detect adulteration. Alone MS is not useful due to complexity of matrix. Chemo-metric is very useful tool in this area [8].

Mass spectrometry application to assess cooking oil quality was reviewed. TAG composition, DAG, MAG, free fatty acids, aldehydes, ketones, epoxides, polymerides and cyclic aromatic hydrogen compounds etc. parameters which influences the quality of cooking oil can be successfully analyzed using mass spectrometry as per review [9].

The highly dynamic technological advancement in instrumentation of mass spectrometers with increasing sensitivity, resolution and speed as well as the integration of orthogonal separation techniques such as ion mobility, capillary electrophoresis and others now allows comprehensive characterization of the complex proteomes of food [10].

Non-targeted screening of chemical contaminants and illegal additives in food based on liquid chromatography & high resolution mass spectrometry has been reviewed favorably [11].

Mass spectrometry-based metabolomics approaches for food safety, quality and traceability was reviewed. Omics is study of all compounds in given system i.e. proteomics is study of all proteins and metabolomics is study of all metabolites present. No single method can successfully applied to all compounds found in food and review put emphasis on using suitable technique for particular group of metabolites. Fingerprint approach does not require any standards nor identification and quantification. Non selective screening tries to identify unknown adulterants. Profiling refers mainly to the analysis of closely related metabolites, often belonging to the same chemical class, which are most frequently identified and quantified. LC-MS is very popular for metabolomics studies. Chemometric is must for analyzing mass spectra [12].

No targeted metabolomics analysis in combination with statistical and machine learning methods can be used to classify samples based on identified patterns. Metabolic fingerprinting technology is rapid but does not necessarily give specific metabolite information. GC and LC MS are popular for these applications. Nowadays QTOF-MS and Orbitrap-based technologies are the most commonly used techniques for non-target screening [13].

Flow injection analysis mass spectrometry (FIA-MS) is technique in which chromatographic separation is not required. FIA-MS offers high-throughput without compromising sensitivity, precision and accuracy as much as ambient MS techniques. Detection limit can go up to PPB and complex matrices like food can be analyzed directly. Generally, FIA-MS sits 'in the middle' between ambient MS and chromatography-MS, offering a balance between analytical capability and sample analysis throughput [14].

In nature, the elements whose isotopic abundance is fit to be used as a tracer for identifying the geographical origin of food are mainly hydrogen, carbon, nitrogen, sulphur and strontium. Hydrogen and oxygen isotopes, are more useful hydrological applications i.e. fish origin. In order to investigate the geographical origin closely linked to the soil, the 87Sr/86Sr isotopic ratio has been successfully measured. Due to its global variability and the numerical range in which it appears, the 87Sr/86Sr isotopic ratio measurement is one very good parameter of origin. It is used for wide range for food products origin tracing. TIMS is always the reference technique for isotopes but there is a growing use of

instruments with an ICP source, in particular the MCICP- MS that shows a measurement precision close to TIMS's, but with very reduced analysis times. Multi collector ICP is sector MS with multiple detectors <sup>[15]</sup>.

### **Milk and Related Products**

Animal milk and soy milk added in human milk as adulterant was detected by using LC-MS and detection was successful at even 5% level. Proteins and lipids are removed from milks i.e. only part of milk constituents are considered for detection. Isotope labeled reagent was added to samples to react with metabolites. Two different isotope labels are used i.e. one with pure components and second with mixture to associate peaks with components <sup>[16]</sup>.

Soybean and pea powder-adulteration in milk was detected at as low as 1% using UPLC-QTF MS using protein as target component. Detection was non targeted using chemo-metric tools <sup>[17]</sup>.

Flow injection mass spectrometry (FIMS) i.e. no chromatographic separation combined with chemometrics was successfully used for detecting economically motivated adulteration of milk with soybean, pea, and whey protein isolates at 0.5, 1, 3, 5, and 10% levels. Detection time was 1 minute and 0.5% detection limits were achieved. The principal component analysis (PCA), partial least-squares-discriminant analysis (PLS-DA), and support vector machine (SVM) classification models are used for classification <sup>[18]</sup>.

A method for quantification of cow's whey and whole milk powder in goat or sheep milk products including infant formula was developed using UHPLC-MS/MS. Detection was based on signature peptides which were predicted to be existing by software given intact protein sequences. Detection limit was 0.01 to 0.05% foreign protein in given product <sup>[19]</sup>.

Mass spectrometry detection of fraudulent use of cow whey in water buffalo, sheep, or goat Italian ricotta cheese was developed. As little as 0.5% bovine whey in ricotta cheese from the other three species can be detected by using whey protein peptide markers <sup>[20]</sup>.

In order to identify the geographical origin of pure milk, different proteins and milk water were extracted from pure milk originated from Australia and New Zealand, Germany and France, the USA, and China. Then,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of the extracted proteins and  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of milk water were determined by element analyzer-isotope ratio mass spectrometry (EA-IRMS). The results indicated that pure milk from these regions could be potentially discriminated by using analyte  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ,  $\delta^2\text{H}$ , and  $\delta^{18}\text{O}$  <sup>[21]</sup>.

### **Oils**

Adulteration of edible oils in sesame oil was detected using ion mobility MS. Random forests and support vector machines are used for identification. Greater than 10% adulteration was identifiable <sup>[22]</sup>.

UHPLC-QTOF-MS has been applied to identify the differentiating chemical markers that allow geographic origin discrimination between different Spanish extra virgin olive oils. Twelve different compounds were found to correctly separate the oils based on their origin. 87% accurate classification was reported using developed method <sup>[23]</sup>.

Suggestion is made that adulteration of edible animal fats with cooked oil can be done by analyzing phytosterols using LC-MS-MS analysis <sup>[24]</sup>. No actual detection was done in study.

Ion mobility spectrometer was used along with UV light as ion generation technique to detect adulteration of vegetable oils in extra virgin olive oil. 10% addition of other oils was detected. PCA-LDA-KNN model was used as statistical tool <sup>[25]</sup>. Note that no quadrupole or TOF etc. mass analyzer was used in this study the ions were separated just based on their mobility.

A certified extra virgin olive oil and refined soybean oil samples were analyzed by direct infusion in ESI MS. Identification of a natural lipid marker present only in soybean oil is done. Even 1% adulteration of soybean oil was detectable. Analysis was completed within 60 seconds <sup>[26]</sup>.

Reversed-phase UHPLC-ESI-QTOF-MS analytical method was developed that uses target, suspect, and non-target screening strategies coupled with advanced chemometric tools for the investigation of the authenticity of extra virgin olive oil. 51 marker compounds were identified. Statistical tools and ANN was used for classification <sup>[27]</sup>.

### **Wines etc.**

Paper spray mass spectrometry and PLS-DA was used to discriminate different beers of similar type but having different prices and thus adulterated in each other. 100% detection correct detection rate achieved <sup>[28]</sup>.

Exogenous addition of sugar and water in the counterfeited table red wines was detected by the measurement of stable isotopes content ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) using mass spectrometry <sup>[29]</sup>.

A fast i.e. no sample preparation and simple method for white wine differentiation based on fingerprinting by means of MALDI combined with linear TOF MS and statistical interpretation of the obtained data using principal component as well as cluster analysis was reported. The method allowed direct comparison and classification of 33 white wines in 7 categories based on peptide mass spectra fingerprints <sup>[30]</sup>.

Multi-dimensional GC in combination with MS-MS is useful for wine authenticity using marker compounds <sup>[31]</sup>. Detection limits was given in terms of concentration of marker compounds which is less useful for rapid understanding.

### **Other Foods**

Peanut allergens detected in chili pepper at 24 ppm level using LC MS MS <sup>[32]</sup>.

Headspace-solid-phase micro-extraction mass spectrometry without any chromatographic separation was used to classify unknown samples of food flavoring essences into two classes corresponding to two similar essences. Statistical methods PCA and PLS-DA was used on peak height at particular m/z ratio and it gave which peaks are important and how much <sup>[33]</sup>.

Closely related adulterant herbal material added in another herbal material was identified and quantified by mass spectrometry-based partial least squares regression. Adulteration detection was possible with and without chromatographic separation but accuracy is improved by separation. UPLC MS-MS approach has given similar results to single UPLC-MS i.e. no improvement possibly due to underutilization of data and due to prior separation has made MS-MS redundant. MS-MS without chromatography was not compared to single MS without chromatography <sup>[34]</sup>.

An analytical method for the reliable screening and confirmation of 156 illegal drugs in supplementary diets using ultra-high-performance liquid chromatography coupled with quadrupole/time-of-flight mass spectrometry was developed.

The wide scope of 156 target compounds was effectively determined within 15 min in single run in the positive ion mode, detecting the compounds at a sub-ppb level [35].

High-performance liquid chromatography (HPLC) and linear-ion trap (LTQ)/Orbitrap high-resolution mass spectrometry were combined to systematically differentiate three mammalian gelatins including bovine-hide gelatin, porcine-hide gelatin and donkey-hide gelatin. Identification was based on marker peptides. It is for done for benefit of Hindus and Muslims [36]. A mass spectrometry method for the determination of the species of origin of gelatin in foods and pharmaceutical products was developed [37].

New protein biomarkers for a targeted detection using LC-MS/MS that can simultaneously prove the presence/absence of garden pea a protein-rich legume, meat and honey and quantify their content in processed vegan food are proposed [38].

Lipids extracts from different rice varieties were analyzed directly using mass spectrometry. Random forests, support vector machines with a radial basis function kernel, C5.0, model averaged neural network, and k-nearest neighbor classifiers were used for the classification. The classifiers effectively differentiated white rice from Korea to blended samples with high prediction accuracy for the contamination ratio as low as five percent. In addition, RF and SVM classifiers were generally found superior to and more robust than the other techniques [39].

Discrimination of American ginseng and Asian ginseng using electronic nose and gas chromatography mass spectrometry coupled with chemometrics was done [40].

Method was developed for the quality control of saffron through the detection and measurement markers compounds by liquid chromatography-quadrupole-time of flight-mass spectrometry [41]. In another study saffron authentication was done to separate it out from other similar flower parts using isotope ratio determination using mass spectrometry. C15 and N15 were used isotopes of choice and up to 5% adulteration was detected [42].

Sugars produced from tropical plants like sugar cane and maize/corn are produced using a photosynthetic pathway referred to as the C4 pathway. Nectar which is collected by bees comes from plants that use a different process of photosynthesis, referred to as the C3 pathway. There is a measurable difference in the ratio of the naturally occurring carbon-12 and carbon-13 isotopes in sugars arising from the C3 and C4 pathways. This has been exploited to detect adulteration of honey either by C3 or C4 sugars by using isotope analysis using chromatography and MS [43].

Simultaneous determination of heat stable signature peptides for eight animal and plant species (pork, beef, lamb, chicken, duck, soy, peanut, and pea) in meat products using UPLC-MS/MS method is done successfully. This can be used for adulteration detection. 0.5% contamination is detectable [44].

Detection of coffee adulteration with soybean and corn flour is done by capillary electrophoresis-tandem mass spectrometry. Monosaccharide profile was used as detection method and hydrolysis was employed to convert poly saccharides in mono saccharides [45].

Rapid detection (no sample preparation) of illegal colorants on traditional Chinese pastries through tandem mass spectrometry with an thermal desorption electrospray ionization source is reported [46].

Spectral database for classification of edible oils using matrix-assisted laser desorption/ionization mass spectrometry was

established and 97 % correct identification was achieved. No especial sample preparation or chromatographic separation was done [47].

Flow Injection ESI-MS technique is used to assess the geographical origin of cocoa beans used to produce chocolate. Asian and African origin of cocoa beans was successfully identified but south American beans was misclassified. KNN classification technique was used. Sample preparation was done i.e. ethanol extraction and filtering. MS-MS was not used [48].

Levels of catechin/epicatechin as phenolics content markers for cocoa content in a series of commercial chocolates was successfully used to estimate cocoa content using MALDI-MS [49].

Aronia berry has a deep red color, and as it is cheaper than blackcurrant, it may be used to adulterate blackcurrant juice and drinks made therefrom. Samples of various blends between the two fruits were analyzed after dilution on UPLC-TOF-MS to create partial least squares (PLS) models. The limit of detection of 5 % aronia berry concentrate in blackcurrant concentrate was achievable [50].

Simultaneous determination of 23 azo dyes in paprika by gas chromatography-mass spectrometry was reported [51]. Screening of over 600 pesticides, veterinary drugs, food-packaging contaminants, mycotoxins, and other chemicals in food by UHPLC-QTOF-MS. This is done in single run. Though most of things were detected below legal maximum limits some were not [52].

Adulteration of papaya seed in black pepper was done using GC-MS and 2% detection limit was obtained. Some studies have suggested that papaya seeds have anti fertility properties and thus this study was important! Finger print approach was used with classification algorithms [53].

Identification of essential oils based on terpene markers and by means of static headspace gas chromatography-ion mobility spectrometry was done. Because head space contain analyte already in gaseous phase no sample preparation is required except mixing to generate vapors if required. Finger print approach was used based on presence or absence of marker compounds but no common statistical method was used [54].

Simultaneous screening and determination of eight tetracycline antibiotics illegally adulterated in herbal preparations is done using HPLC-DAD combined with LC-MS-MS. Detection range was 1-25 µg/ml [55]. Note that DAD detectors can detect absorption at all wavelengths simultaneously.

Fish fraud detection is mainly carried out using a genomic profiling approach requiring long and complex sample preparations and assay running times. Rapid evaporative ionization mass spectrometry (REIMS) can circumvent these issues without sacrificing a loss in the quality of results. No sample preparation is involved in this technique. 99% correct identification achieved for genetically similar fish and each identification takes just 2 seconds and thus this technique can be claimed real time. Orthogonal partial least squares-discriminant analysis was used for classification [56].

## Conclusion

Mass spectrometry is very powerful technique for adulteration detection and almost any conceivable adulteration can be detected and quantified by it provided the samples are separated using GC or LC to reduce effect of matrix substances. MS techniques without chromatography are being

developed actively and at present time they are sufficient for detection purposes but they struggle in quantification as they face competition from chromatography MS cousins. Determination of concentration even without prior separation is better than many ordinary methods in many cases. For methods, with chromatographic or similar separation, initial cost of machine as well as running cost is high. Orbitrap MS has highest sensitivity while quadrupole MS is cheapest.

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