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Comprehensive Chemical Fingerprinting of Bean, Onion and Potato Using Non-Targeted GC–MS: QuEChERS Extraction, NIST Library Identification and Applications in Food Quality Assessment

Abstract

Beans, onions, and potatoes are nutritionally important food crops with complex chemical compositions comprising carbohydrates, proteins, amino acids, organic acids, fatty acids, phenolics, sterols, sulfur-containing compounds, volatile constituents, and other specialized metabolites. Their chemical profiles vary considerably with cultivar, geographical origin, agricultural practices, maturity, storage, and processing conditions, making comprehensive chemical fingerprinting valuable for nutritional evaluation, quality assessment, authentication, and food-safety monitoring. Conventional targeted methods provide accurate analysis of predefined compounds but may overlook unexpected or previously unidentified constituents. Non-targeted metabolomic approaches overcome this limitation by providing a broader representation of the chemical composition of food matrices. Gas chromatography–mass spectrometry (GC–MS) is particularly suitable for profiling volatile and semi-volatile compounds because of its high chromatographic resolution, reproducible mass spectra, and extensive spectral-library resources. QuEChERS extraction provides a rapid, simple, and efficient sample-preparation approach for complex vegetable matrices. This review examines the application of QuEChERS-assisted non-targeted GC–MS for chemical fingerprinting of bean, onion, and potato, emphasizing metabolite profiling, NIST library identification, retention-index confirmation, and chemometric analysis. Applications in cultivar discrimination, authentication, storage, processing, contaminant screening, and food-safety assessment are discussed. Future integration with GC×GC–MS, LC–

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MS, NMR, and machine-learning approaches may further improve comprehensive food fingerprinting and chemical characterization.

Keywords: Bean; Onion; Potato; Chemical fingerprinting; Non-targeted GC–MS; QuEChERS; NIST library; Metabolomics; Food quality; Food safety

1. Introduction

Food quality assessment has traditionally relied on targeted analytical methods designed to quantify a predefined group of compounds, such as pesticide residues, vitamins, pigments, phenolics or specific contaminants. Although targeted methods provide excellent quantitative accuracy, they are inherently restricted to compounds selected before analysis. Consequently, unexpected metabolites, degradation products, adulterants or unknown contaminants may remain undetected. Non-targeted metabolomic profiling addresses this limitation by attempting to capture a broad chemical representation of a sample and subsequently interpreting differences among samples (Dunn et al., 2011). This approach is particularly valuable for investigating food authenticity, geographical origin, cultivar differentiation, spoilage, processing effects and unexpected chemical contamination.

Among analytical platforms, gas chromatography–mass spectrometry (GC–MS) remains one of the important techniques for food metabolomics and chemical fingerprinting. GC provides high chromatographic resolution, whereas electron-ionization (EI) mass spectrometry generates reproducible fragmentation patterns that can be compared with reference spectral libraries. The NIST Mass Spectral Library and associated retention-index resources therefore provide an important foundation for tentative identification of GC–MS features (Stein, 1999; NIST, 2023). The NIST23 release further expanded the available spectral resources and included updated electron-ionization and retention-index databases (National Institute of Standards and Technology [NIST], 2023).

Sample preparation is another critical component of non-targeted food analysis. Conventional extraction procedures can involve multiple transfers, large solvent volumes and extensive purification steps. The QuEChERS approach was introduced by Anastassiades et al. (2003) as a rapid multiresidue pesticide-extraction procedure based on acetonitrile extraction, salt-assisted partitioning and dispersive solid-phase extraction. The original procedure used acetonitrile followed by magnesium sulfate and sodium chloride partitioning and was developed specifically for pesticide analysis in produce.

Since its introduction, QuEChERS has been modified through the use of buffered extraction systems and different dispersive-SPE sorbents. These modifications have expanded its applicability to a broad range of food contaminants and chemical classes (Lehotay et al., 2010; Rejczak & Tuzimski, 2015; Perestrelo et al., 2019). Importantly, the simplicity and broad extraction capability of QuEChERS make it attractive for fingerprinting applications in complex matrices.

Bean, onion and potato provide useful examples for evaluating this analytical strategy because they possess chemically distinct signatures. Bean contains abundant fatty acids, sterols, carbohydrates and nitrogen-containing metabolites, onion is particularly rich in reactive organosulfur compounds, and potato contains starch, organic acids, reducing sugars and steroidal glycoalkaloids.

The objective of this review is therefore to critically discuss the use of QuEChERS extraction coupled with non-targeted GC–MS and NIST spectral-library identification for comprehensive chemical fingerprinting of bean, onion and potato. The review focuses on sample preparation, GC–MS acquisition, compound identification, characteristic chemical classes, chemometric analysis, food-quality applications, limitations and future perspectives.

2. Analytical Framework: QuEChERS–GC–MS–NIST Workflow

2.1 QuEChERS Extraction

The QuEChERS procedure generally consists of extraction/partitioning followed by dispersive solid-phase extraction cleanup. In the original method, homogenized food is extracted using acetonitrile, followed by addition of magnesium sulfate and sodium chloride to promote phase separation and water removal. The organic phase can subsequently undergo dispersive-SPE cleanup using sorbents such as primary secondary amine (PSA) and, when appropriate, graphitized carbon black (GCB) or C18 (Anastassiades et al., 2003; Lehotay et al., 2010).

For non-targeted fingerprinting, however, the objective differs from conventional pesticide-residue analysis. Excessive cleanup can remove compounds that may be chemically informative. Therefore, optimization should focus on achieving a compromise between matrix reduction and maximum chemical coverage. Buffered QuEChERS variants may be useful for pH-sensitive compounds, whereas reduced GCB treatment may help preserve pigment-associated and planar aromatic metabolites.

For GC analysis of highly polar metabolites, derivatization may be necessary. Silylation using reagents such as MSTFA or BSTFA can increase volatility and thermal stability of sugars, organic acids and other polar compounds. Nevertheless, derivatization introduces another source of analytical variability and must therefore be carefully standardized.

2.2 GC–MS Acquisition

A typical GC–MS fingerprinting experiment employs a non-polar or moderately polar capillary column, helium as carrier gas, electron ionization at approximately 70 eV and full-scan acquisition. Full-scan acquisition is particularly important in non-targeted analysis because selected-ion monitoring would restrict the dataset to predefined ions.

Retention indices (RIs) provide an important complementary identification parameter. Co-injection or separate analysis of an n-alkane series can allow experimental RIs to be calculated and compared with literature or library values. Consequently, reliable annotation should preferably consider both mass spectral similarity and retention behavior, rather than relying solely on the library match.

2.3 NIST Library-Based Identification

Following chromatographic separation, mass spectra can be deconvoluted and compared with reference spectra in the NIST/EPA/NIH Mass Spectral Library. The NIST resources provide extensive mass spectral and gas-chromatographic information that can assist compound annotation (NIST, 2023).

However, a high library match should generally be interpreted as a tentative identification rather than absolute structural confirmation. Similar EI fragmentation patterns can occur among isomers or closely related compounds. Therefore, identification confidence should ideally incorporate: spectral similarity; forward and reverse library match; retention-index agreement; chemical plausibility; and authentic-standard confirmation where available. This is particularly important for chemically reactive compounds and structural isomers. The uploaded draft appropriately emphasizes that spectral similarity and retention behavior together reduce the risk of false-positive annotation.

3. Chemical Fingerprint of Common Bean (*Phaseolus vulgaris*)

Beans contain a complex mixture of primary and secondary metabolites. GC–MS-based fingerprinting may reveal fatty acids, fatty-acid esters, lipid-oxidation products, sterols, organic acids, sugars and nitrogen-containing volatile compounds.

Table:1 Major chemical classes

Compound class	Representative compounds	Analytical significance
Fatty acids	Palmitic, linoleic, linolenic and oleic acids	Lipid composition and oxidative stability
Volatile aldehydes/alcohols	Hexanal, nonanal, 1-hexanol	Oxidation and storage markers
Phytosterols	β-Sitosterol, stigmasterol, campesterol	Nutritional and authenticity markers
Nitrogen volatiles	Methylpyrazine, dimethylpyrazines	Processing/Maillard markers
Organic acids	Citric, malic and succinic acids	Metabolic and cultivar differences
Sugars/oligosaccharides	Sucrose, raffinose and stachyose	Nutritional and digestibility-related characteristics

The chemical fingerprint of bean can change substantially during cooking, roasting, fermentation and germination because these processes modify lipid oxidation and Maillard chemistry. Consequently, GC–MS fingerprints may provide useful information regarding processing history and storage conditions. The uploaded draft similarly identifies pyrazines, Strecker aldehydes and lipid-derived volatiles as important processing and storage-related features.

4. Chemical Fingerprint of Onion (*Allium cepa*)

Onion has one of the most distinctive chemical fingerprints among common vegetables because of its abundance of sulfur-containing compounds. When onion tissue is cut or damaged, S-alk(en)yl-L-cysteine sulfoxides undergo enzymatic transformation, producing reactive sulfur intermediates and volatile compounds responsible for onion aroma and pungency (Block, 1992). Important chemical groups include thiosulfinates, sulfides, disulfides, trisulfides, thiophenes, flavonoids and sugars. Dipropyl disulfide, dipropyl trisulfide and related sulfur compounds can contribute to the characteristic aroma profile. Recent analytical work has emphasized that onion organosulfur profiling can benefit from combining GC-based approaches with high-resolution LC–MS because some reactive

or non-volatile sulfur compounds may not be fully represented by conventional GC analysis (González-de-Peredo et al., 2024). Furthermore, recent literature continues to demonstrate the substantial chemical diversity and biological relevance of onion organosulfur compounds (Tang et al., 2026). Because these compounds can be highly reactive, sample handling is particularly important. Headspace or SPME approaches can complement liquid extraction when the objective is to characterize the native volatile fraction. The uploaded draft highlights the possibility of thermal artifact formation during conventional hot GC injection and recommends complementary volatile sampling.

5. Chemical Fingerprint of Potato (*Solanum tuberosum*)

Potato is chemically dominated by starch, sugars and organic acids, but several specialized metabolites are particularly important from a food-safety perspective. Among these, the steroidal glycoalkaloids α-solanine and α-chaconine are major diagnostic compounds. Potato glycoalkaloids are associated with plant defence and can increase under conditions such as greening and physical stress (Friedman, 2006). Because intact glycoalkaloids are relatively polar and thermally unsuitable for direct GC analysis, GC-based approaches may require hydrolysis and derivatization. This illustrates an important limitation of GC–MS fingerprinting: although the technique offers excellent coverage of volatile and derivatizable metabolites, highly polar or thermally labile compounds may be better characterized by LC–MS.

Other important potato fingerprint components include fatty acids, lipid-derived aldehydes, organic acids, reducing sugars and amino-acid-related metabolites. In particular, the concentrations of reducing sugars and free asparagine are important in relation to acrylamide formation during high-temperature processing. Friedman (2004, 2006) provided extensive reviews of potato bioactive compounds and glycoalkaloids, establishing the importance of these metabolites for nutritional and food-safety evaluation.

Table:2 Comparative Chemical Fingerprints

Commodity	**Dominant diagnostic chemistry**	**Important analytical consideration**
Bean	Fatty acids, phytosterols, lipid-oxidation volatiles, pyrazines	QuEChERS extraction with appropriate cleanup; derivatization for sugars and organic acids
Onion	Organosulfur compounds, sulfides, disulfides, flavonoids	Minimize thermal artifacts; consider headspace/SPME and complementary LC–MS
Potato	Glycoalkaloids, sugars, organic acids, fatty acids, Maillard precursors	GC derivatization/hydrolysis may be required; LC–MS can complement GC–MS

The comparison demonstrates why a single extraction and analytical strategy should be optimized according to the chemical characteristics of each commodity rather than applied without modification.

6. Chemometric Interpretation of GC–MS Fingerprints

Non-targeted GC–MS generates large datasets containing numerous chromatographic features. Data preprocessing generally includes baseline correction, peak detection, deconvolution, retention-time alignment, normalization and feature filtering. Chemometric approaches can then convert complex peak tables into interpretable patterns. Principal component analysis (PCA) is useful for unsupervised visualization of sample clustering, whereas hierarchical cluster analysis can reveal similarities among samples. Supervised techniques such as partial least-squares discriminant analysis (PLS-DA) can be used for classification when predefined sample groups exist. Food-authentication studies have demonstrated the usefulness of combining chromatographic fingerprints with chemometric models for geographical and authenticity discrimination. However, model validation is essential because supervised models can overfit when sample numbers are small relative to the number of measured features. Therefore, cross-validation, independent test sets and appropriate statistical significance testing should be incorporated before claiming classification performance.

7. Applications in Food Quality and Safety

7.1 Authentication and Adulteration Detection

The complete GC–MS profile can function as a multidimensional chemical barcode. Rather than relying on a single marker, the entire pattern of metabolites can be used to differentiate cultivars, species, geographical origins and potentially adulterated samples.

7.2 Freshness and Storage Monitoring

Volatile lipid-oxidation products such as hexanal and nonanal may increase during storage and can provide indicators of oxidative deterioration. In potato, glycoalkaloid accumulation can additionally provide information regarding inappropriate storage and greening.

7.3 Cultivar and Geographical Discrimination

Differences in flavonoids, sterols, sulfur-containing compounds, sugars and other metabolites may provide chemical markers for cultivar differentiation and geographical authentication.

7.4 Pesticide Residue Screening

QuEChERS was originally developed specifically for multiresidue pesticide analysis in fruits and vegetables (Anastassiades et al., 2003). Therefore, the same general extraction concept can be adapted for pesticide screening alongside broader fingerprinting. However, regulatory pesticide determination requires validated quantitative methods, calibration, recovery experiments and appropriate quality-control procedures.

7.5 Processing and Cooking Assessment

Changes in pyrazines, aldehydes, sulfur compounds and other volatile constituents can provide chemical evidence of cooking, roasting, frying, fermentation or dehydration. Such fingerprints may therefore assist industrial process control.

8. Future Perspectives

Future research should focus on improving both chemical coverage and identification confidence. GC×GC–MS can provide enhanced separation of complex mixtures and may be particularly useful for highly complex volatile fractions. Combination of GC–MS with LC–MS can expand coverage to both volatile/derivatizable and non-volatile metabolites. The recent onion literature illustrates the value of combining GC and LC high-resolution MS for more complete characterization of organosulfur chemistry (González-de-Peredo et al., 2024).

Development of commodity-specific spectral libraries containing both mass spectra and retention indices could further improve identification. Machine-learning methods may also allow integration of chemical fingerprints with hyperspectral imaging, sensory measurements and environmental information for rapid food-quality screening.

9. Conclusion

Bean, onion and potato possess chemically diverse profiles that reflect their genotype, cultivation conditions, maturity, storage and processing history. Non-targeted GC–MS provides a powerful platform for detecting a broad range of volatile and semi-volatile metabolites, while QuEChERS offers a rapid and efficient extraction strategy for complex food matrices. NIST spectral libraries facilitate tentative identification of GC–MS features, particularly when combined with retention-index information and authentic standards. The chemical fingerprints of the three commodities are distinctly different: beans are characterized by lipid-derived compounds, sterols and nitrogen-containing volatiles; onions possess a highly distinctive organosulfur profile; and potatoes contain characteristic glycoalkaloids, sugars, organic acids and lipid-derived compounds. These differences make QuEChERS–GC–MS fingerprinting useful for cultivar differentiation, authentication, storage monitoring, processing assessment and broad food-safety screening. Nevertheless, non-targeted GC–MS should not be considered a replacement for validated targeted methods when regulatory quantification is required. The strongest analytical strategy is therefore a tiered workflow, in which non-targeted GC–MS is used for broad screening and fingerprint discovery, followed by targeted confirmation using authentic standards and validated quantitative procedures. Integration of QuEChERS extraction, non-targeted GC–MS, NIST library searching, retention-index confirmation and chemometric analysis provides a promising framework for comprehensive chemical characterization of bean, onion and potato and can contribute significantly to modern food-quality, authenticity and safety assessment.

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