GC-MS fingerprinting for food authenticity evaluation

Identification

Key words
GC-MS, fingerprinting, non-targeted analysis, multicomponent analysis, chemometrics, multivariate data analysis, food authenticity evaluation, food adulteration, food falsification

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How does it work?

Primary objective
Advanced analytical tool enabling unbiased comparison/classification of food samples, based on the volatilizable fraction of the food.
Working principle

In a conventional gas chromatography - mass spectrometry (GC-MS) approach, compounds are identified (i.e. targeted analysis) prior to their, often relative, quantification and subsequent comparison between the biological samples. A fingerprinting approach (see Figure) is characterized by unbiased (i.e. non-targeted analysis), multicomponent analysis of complex biochemical datasets, in which first a discriminative data-analysis is performed, followed by selection of specific fingerprinting markers, after which these markers can be studied using a profiling approach. Fingerprint markers are these compounds with are responsible for the different grouping of samples. In other words, the compounds which are specific for a group compared to the other groups (e.g. a compound which is only detected in these group or a compound which is specifically detected in a higher or lower amount in this group). These compounds are very interesting for food authentication. For example, if grapes from Italy have a specific aroma compound compared to grapes of France, it can be interesting to just evaluate this fingerprint marker in order to define from with origin the grapes are. Instead of comparing the complete fingerprint, only comparison of the fingerprint marker between batches can be sufficient to determine authenticity. Optimizing analytical conditions for GC-MS fingerprinting purposes, detection of as many as possible different peaks will be aimed at.

![Figure: Schematic description of the different steps necessary for comparative analyses of food by GC-MS fingerprinting. After selection of specific compounds for each food product class, GC-MS data can be used for food profiling.](image)

In a first step, a representative food extract need to be obtained: (i) For headspace extraction, a particular equilibrium between the gas and liquid/solid phase of the food is intended. Too high temperatures (resulting in food product reactions) during this equilibration phase should be avoided at all times. The gas phase can be directly extracted using static headspace (using a syringe) or solid phase micro extraction (SPME), using a specific fibre. Methods based on headspace extraction, are so-called semiquantitative due to the presence of a matrix effect and relatively short linearity of the dynamic phase. (ii) Chemical derivatization (2) can be used for, for example, influencing the volatility of compounds or reducing the polarities of functional groups, facilitating their separation by GC. It should be noted that derivatization steps add time and complexity to sample preparations and introduce an additional source of variance to the experimental procedures. As derivatization by definition induces chemical changes and is sometimes performed under harsh conditions with a consequent risk of artifact formation, it is best avoided if at all possible.

In a next step, the extract is injected in the GC-MS injection port. In GC-MS fingerprinting, comparative analysis occurs at the level of peaks and not at the level of molecular fragments when direct analysis mass spectrometry is used, thereby including an additional dimension (chromatographic retention factor) and decreasing the number and the chemical diversity of compounds simultaneously entering the mass spectrometer at a particular moment enabling further characterization and differentiation. However, co-elution of comp
Fingerprint markers (specific for for instance processed food, ....) are extremely interesting to be studied in more detail. For these compounds, identification and quantification is very relevant (profiling; see Figure). For identification of compounds detected by GC-MS, commercially available MS libraries for automated matching (e.g. NIST 02, Wiley) are frequently used. Such automated matching cannot be entirely relied upon and data must be checked by an experienced analyst in order to ensure the integrity of the results: a daunting task when one considers the amount of data produced in a short time by modern hyphenated techniques.

The volatilizable fraction will be extracted by incubation under particular temperature, time conditions or by chemical derivatization. Independently of the extraction method chosen, this needs to be optimized matrix per matrix. To select to appropriate extraction conditions per matrix, it can be important to vary the polarity of the extraction buffer or to test the difference in affinity between the volatilizable fraction and the coating material of the SPME fibers. Today, several coating materials of fibers are available.

In fingerprinting analyses (i.e. discriminative analyses), at all times, analysis parameters (e.g. type of SPME fiber, GC-column, ...) should be selected aiming at detection a wide range of components.

All food products as they are always characterized by a considerable volatilizable fraction.

- Identification of region-specific characteristics of crops (4,7)
- Identification of botanical-specific characteristics of crops (4)
- Tracing wine adulteration (4)
- Identification of seasonal-specific characteristics of crops
- Classification/discrimination of wines, honey, tea, oils, beer, ... (1)
- Metabolomic analysis in food science (3,5,6)
- Evaluation of the substantial equivalence of novel foods
- Impact comparison between different processing technologies

• Non-targetted (i.e. unbiased) comparison of food samples
• Authenticity evaluation of a food product
• Fast screening method for particular compounds

None

• high investment equipment, but lower investment than LC-MS or LC-NMR.
• GC-MS can only be used to analyze the volatilizable fraction.
• co-elution of compounds has been frequently reported
• one of the principal disadvantages of chromatographic techniques relates to their use in conjunction with chemometrics (multivariate data analysis such as principal component analysis, (orthogonal) partial least squares-discriminant analysis, soft independent modelling of class analogy). The use of chemometrics is not generally known, nor low barrier. In addition, it can be time and labour intensive.
• analytical techniques are characterized by a detection limit. Consequently, detection of no differences does not mean that no differences existed in the volatilizable fraction.
Risks or hazards

Columns are acting as filters and not all components injected will necessarily pass through. This is in stark contrast to a non-destructive spectroscopic technique such as NMR. The analyst must therefore be aware and appropriate controls must be incorporated in any of such analytical systems. Of course, when health-endangering chemicals are used the necessary precautions should be taken.

Implementation

Maturity

Analysis tool is available, but the method should be optimized matrix per matrix.

Modularity /Implementation

This analysis methodology is destructive. The main challenge in implementation is data analysis. It requires well-trained personnel.

Consumer aspects

Not applicable. It will be in the consumers’ interest that fingerprinting methods are available for fast screening of authenticity of food products.

Legal aspects

None. GC-MS fingerprinting for authenticity evaluation is a methods that received important interest by legislator affairs.

Environmental aspects

Solvents used for chemical derivatization are environmentally unfriendly.

Facilities that might be interesting for you

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<th>Title</th>
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<td>Field Flow Fractionation INPT - EI Purpan</td>
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<td>Fruit &amp; vegetable analysis INRA</td>
<td>INRA - SQPOV</td>
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<td>Gas analysis INRA</td>
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Further Information

Institutes

KU Leuven LFT, IFR, Wageningen UR - PRI, RIKILT, Royal Holloway - Biol. Sci., University College Dublin

Companies
References


Source: