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Review

The volatile metabolome – gas chromatography–mass spectrometry approaches in the context of food fraud Beatriz Quintanilla-Casas¹, Berta Torres-Cobos^{2,3}, Rasmus Bro¹, Francesc Guardiola^{2,3}, Stefania Vichi^{2,3} and Alba Tres^{2,3}



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Food fraud: definition, present state, and current gaps

Food fraud is a complex problem, prompting many definitions to identify its elements and, more importantly, to determine what is needed to solve it in the current context [1]. Despite slight differences, key criteria are present in all definitions of food fraud: (1) Violation of the corresponding food law, (2) full intentionality, (3) economic gain, and (4) customer deception. For a case to be classified as food fraud, all four elements must be met. While economic motivation is the primary driver behind food fraud practices, these acts pose a public health threat of uncertain magnitude. Food safety concerns are generally associated with adulteration, especially because of emerging adulterants that evade the current food protection system [2]. Nevertheless, the lack of traceability in any fraudulent food product including counterfeiting and mislabelling — can also present a health risk to consumers.

According to the criminalistic approach of food fraud defined by Spink and Mover [3], fraud opportunities can be significantly reduced by implementing efficient control measures. The 2022 annual report of the Alert and Cooperation Network within the European Commission highlights gaps in food fraud control by showing the food categories with high number of notifications, as well as the fraudulent practices most frequently encountered, affecting more than one country [4]. This is the closest approximation for quantifying food fraud cases, as many instances go unnoticed. The top five notified food categories are 'Honey & royal jelly', 'Live animals', 'Meat & meat products', 'Fish and products thereof', and 'Fats & oils'. The most notified agri-food fraud categories and subcategories are shown in Figure 1, standing out 'Substitution (Adulteration/product tampering)', followed by 'Mislabelling', which includes false quality terms and geographical claims. Finally, related to counterfeit, some notified cases involved Protected Designations of Origin and Protected Geographical Indications. Current official authentication methods rely on analytical techniques where one or few compounds are investigated to distinguish authentic from nonauthentic products. Unfortunately, fraudsters often stay a step ahead of control methods by exploiting the low efficiency of certain





Notifications by agri-food fraud categories and subcategories [6].

methods, the lack of sensitivity of some techniques, for example, limits of quantification; or the fact that methods focus on a single compound or compound family. Additionally, for certain commodities like virgin olive oil, verifying the declared commercial category involves assessing sensory quality through a panel test procedure, which may present drawbacks such as limited sample assessments per day and inconsistencies among panels [5]. Therefore, being up to date about the state-of-the-art fraudulent practices is key to develop fit-for-purpose authentication methods. Developing optimal authentication methods requires several elements: selecting reliable chemical markers for the intended purpose, measuring them through a high-throughput yet affordable analytical technique, and applying suitable chemometric methods to build effective authentication tools.

Food volatile metabolome: definition and implications in food quality and authenticity

The volatile metabolome refers to the array of volatile organic compounds (VOCs) produced in foods through various chemical or metabolic pathways. These compounds may originate from raw materials, influenced by factors such as species, geographic origin, and other variables, or they may form during processing and storage via chemical or enzymatic reactions, or through microbial metabolism. Consequently, they serve as diagnostic markers for various aspects of the food product, including the type, quality, and origin of raw materials, as well as the processing and storage conditions, factors often considered critical for food quality and authenticity. These VOCs, characterized by their small molecular size and propensity to vaporize at room temperature, significantly contribute to the aroma profiles of foods [6]. Consequently, they serve as ideal markers for instrumentally assessing or verifying sensory attributes and overall food quality. For this reason, the volatile metabolome of a various food products has been extensively studied in recent years, particularly those favored by consumers for their hedonic value, such as wine, olive oil, and coffee [7].

Detecting food fraud through volatile metabolome analysis

Volatile metabolome as authentication marker

The gold standard for food authentication markers is their direct relation with the feature being authenticated. Certain VOCs are responsible for both quality sensory attributes, such as fruitiness in virgin olive oils [8], and undesirable off-flavors, such as off-odors in fish [9]. This is why VOCs and the volatile metabolome have been reported as useful for assessing sensory quality. Assessing VOCs has proven valuable in global sensory evaluation, such as verifying the commercial categories of virgin olive oil [10,11], and in predicting specific attributes derived from endogenous VOCs or those generated during processing and storage, as recently reviewed by Díez-Simon et al. [12].

Besides, the VOC metabolome is influenced by various factors such as seasonal variation, geographical origin, feeding regimes, and storage conditions [13], which is a blessing and a curse. On the one hand, this apparently offered possibilities of using VOC to diagnose various food characteristics such as the geographical or varietal origin. In fact, promising results were reported in works that tested VOCs as geographical markers [11,14-18]. However, as mentioned above, some VOCs may be greatly affected by processing and storage conditions [5], compromising the long-term stability of models authenticating quality aspects unrelated to sensory quality. Consequently, in these cases, it would be advisable to base models only on stable VOCs that are less prone to undesired profile modifications during processing and storage. Recent studies have revealed that semi-volatile sesquiterpene hydrocarbons (SHs), secondary plant metabolites, are stable and valid markers for botanical and geographical authentication of certain food products [19-22].

Instrumental assessment of food volatilome: sample preparation and analytical technique

Sample preparation is a critical step when measuring VOCs; therefore, several sampling techniques have been reported. Nonextraction techniques, such as static

headspace, might not be ideal for food samples, given the presence of key VOCs at trace levels. Among the sampling techniques involving VOC extraction, such as dynamic headspace, purge and trap or stir-bar sorptive extraction, solid phase microextraction (SPME) has emerged as the predominant method in several food matrices [23]. Proven robust in recent collaborative studies on virgin olive oil [24], this solvent-free, automatable technique requires minimal investment and is well suited for control purposes.

An important aspect to consider when evaluating the applicability of an authentication tool as a control method is the availability and affordability of the instrumental technique. Gas chromatography coupled to mass spectrometry (GC-MS) is among the main analytical techniques to measure the VOC profile of different kinds of samples, including food products. In addition to its high sensitivity and widespread availability in routine laboratories, GC-MS offers comprehensive molecularlevel information through three-way data (an array of intensity × retention time × m/z for each sample). This allows for more reliable compound identification in targeted approaches and enhances the efficiency of untargeted-based modeling compared to other detection techniques, such as flame ionization detectors. Using high-resolution MS instead of conventional low-resolution quadrupolar and ion trap mass analyzers offers improved sensitivity and more reliable identification through exact mass measurements. This enables the detection of trace VOCs, which is crucial for differentiating authentic from nonauthentic food products. Despite its potential for food authentication through VOC assessment [25], high-resolution MS remains financially inaccessible for many control laboratories.

Data analysis approaches

From targeted to untargeted methods

Conventional methods for food analysis, including VOC assessment, are based on targeted methods. These involve the identification and quantification, or semiquantification by an internal standard, of one or few predefined chemicals (Figure 2a). The conformity of the product to a given standard depends on whether the resulting values are above or below an established limit. This strategy is known to be robust, straightforward to transfer and follows well-established validation schemes [26]. The time-consuming step of identification, quantification, and manual data extraction involved in target approach can be facilitated by in silico tools for GC-MS data analysis (Figure 3). These include proprietary toolboxes such as ChemStation (Agilent), ChromaTOF (LECO) MassLynx (Waters corporation), or MassHunter (Agilent), as well as open toolboxes such as AMDIS, pyMS, and XCMS [27,28]. After peak identification, the mass spectra of identified peaks are usually matched





Summary of targeted and untargeted methods applied to chromatography: (a) single/dual-targeted approach, (b) targeted profiling, (c) untargeted profiling, and (d) fingerprinting (B Quintanilla-Casas, PhD thesis, University of Barcelona, 2022).

with commercial or in-house spectral libraries to find the corresponding chemical structures. However, beyond workflow optimization, valuable information is lost in targeted approaches since only a small part of the analytical signal is used [26,28]. This fact triggers fraud opportunity because adulteration is way more difficult to detect, as long as the targeted compound stays within the boundaries. The so-called targeted profiling enhances the efficiency of control methods by selecting a priori multiple target compounds for identification and quantification (Figure 2b) [26]. In the context of using the volatile metabolome to detect food fraud, the targeted approach has been successfully applied to assess the sensory quality of virgin olive oil, aimed at complementing the official panel test method [11,24]. Yet, the inconveniences related to the cumbersome identification and integration of analytes, related to detection limits or chromatographic coelution, become more pronounced as the number of compounds under consideration increases. Additionally, when measuring authentication markers such as SHs, the targeted identification is hindered by the similarity of their mass spectra, which causes that many SHs have not been consistently identified yet [29]. As reviewed by Xu et al.

[30], despite targeted analysis that might be more sensitive for fruit juice authentication, untargeted methods would be more effective when the fraudulent practice we face remains unclear.

For these reasons, untargeted (or nontargeted) methods are gaining importance in food authentication. On the one hand, the untargeted profiling analysis simultaneously semi-quantifies a high number of not predefined compounds — often > 100 [26] — (Figure 2c). As previously mentioned, GC-MS data correspond to a threeway array (Figure 4a); therefore, this approach could benefit from advanced data analysis tools to translate the analytical signal into peak tables with the corresponding chemical information. Unlike the above-mentioned toolboxes for GC-MS data analysis, which can also be applied for untargeted approaches, PARAllel FACtor analysis 2 models stand out due to the ability to automatically deconvolute peaks across all samples, including those with retention time shifts, low signal-tonoise ratios, or co-eluted compounds [27]. Moreover, its integration and automatization through the software PARADISe (PARAllel factor analysis 2 Deconvolution and Identification System) increases the robustness of





the results due to the lack of user interaction while optimizing the analysis time [31]. This software has been successfully applied on VOC data to assess the quality and authenticity of different foods [8,32,33].

On the other hand, the state-of-the-art strategy in food authentication involves finding specific patterns in the analytical fingerprint, thus introducing the untargeted fingerprinting approach [34] (Figure 3). Some authors consider fingerprints as the compilation of multiple analytical parameters [26] or molecular markers [34], while others define it as the analytical outcome of a single technique [35]. The former definition agrees better with the untargeted profiling approach; therefore, the term fingerprint should refer to the set of data points composing the raw analytical signal (Figure 2d; B Quintanilla-Casas, PhD thesis, University of Barcelona, 2022). Three-way data, such as the GC-MS output, typically require complex multiway chemometric algorithms. Nevertheless, they can be transformed into twoway data to enable the application of bilinear methods. This can be achieved either by using the total ion chromatogram (Figure 4b) [10,36] or by unfolding the original array through the extraction and concatenation of all or some of the acquired m/z (Figure 4c), as proposed in recent studies on food volatile metabolome [20,29]. In any case, chromatographic fingerprints need alignment to correct retention time shifts among samples, an inherent issue in chromatography. This can be done through different techniques, ranging from the most rigid, like correlation optimized shifting (coshift) or less rigid extension by intervals (icoshift), to more flexible methods that shift, stretch, and/or compress profiles without swapping peaks, like correlation optimized warping [37]. Classification models constructed with aligned chromatographic fingerprints have provided successful results for several food authentication problems [10,19,20,29,36,38,39]. Specifically, the fingerprinting approach has proven significantly more efficient than profiling when assessing the origin of virgin olive oil based on SHs data, thanks to its comprehensive use of analytical information [29]. Nevertheless, it is important to note that models developed from fingerprinting approaches may be more susceptible to overfitting than other methods if proper modeling practices and validation techniques are not adhered to.

Chemometrics in food authentication

Despite resulting in more efficient authentication models [29,30], moving from conventional targeted to novel untargeted methods requires multivariate chemometric methods to effectively process and extract the information from complex chromatographic data.

Classification methods are the most prevalent supervised machine learning techniques in food authentication [13], particularly when the goal is developing screening tools to detect potential fraudulent samples (Figure 3). Among these, discriminant and class-modeling techniques are applied for authentication purposes based on the volatile





From three-way to two-way data in chromatography coupled to MS (one sample). *m/z*: mass/charge ratio (B Quintanilla-Casas, PhD thesis, University of Barcelona, 2022).

metabolome [36,38]. In discriminant techniques, samples are classified into one of the predefined classes, whereas class-modeling techniques focus on a single class and determine whether samples belong to that class. The main representative of the former group is partial least squares-discriminant analysis (PLS-DA). PLS-DA seeks for maximizing the covariance between the latent variables resulting from variable reduction of a given data matrix and the response variable, which is a dummy variable identifying the different classes, regardless of being a binary or multiclass authentication problem [40,41]. PLS regression is also commonly applied when aiming at a quantitative prediction of a numeric response variable for authentication purposes [13]. Among class-modeling techniques, soft independent modeling of class analogy (SIMCA) is one of the most applied methods [42]. SIMCA models are based on principal component analysis (PCA) for each of the categories. They are often called one-class methods since they focus on a well-represented category of samples rather than multiple classes. PLS, instead, is generally applied to build multiclass models through PLS-DA. However, the extension one-class PLS could be used for a similar aim than SIMCA, although its use on VOCs has not been reported for authentication so far. On the other hand, supervised nonlinear classification

methods based on, for example, artificial neural networks, support vector machine, or random forest have also been explored for authentication purposes using the volatile metabolome [43,44]. Model interpretability still remains a challenge for nonlinear methods due to their complexity, nonlinear relationships, and intricate model structures, which also complicates visualization. Contrarily, linear methods make it easier to identify relevant variables, even in untargeted approaches. This enables the identification of specific VOCs relevant to a particular class, ensuring the model does not function as a 'black box' [10,29].

When developing authentication tools, achieving a high performance in classification becomes a priority. Threshold optimization strategies such as the application of receiver operating curves (ROC) might reveal the thresholds leading to optimal sensitivity and specificity, but the definition of the decision criteria may depend on the intended use of the authentication method. For instance, VOC fingerprinting was suggested as a screening method to detect boundary samples in olive oil sensory quality evaluation whose identity would be further confirmed by a sensory panel test [36].

Besides supervised models, previous works also focused on unsupervised machine learning tools such as PCA, usually to explore trends within the analytical data, as well as clustering methods [13]. Nevertheless, the reduced matrix consisting of few principal components is sometimes not enough to explain the variance within different categories in authentication problems, especially when chromatographic fingerprints are used.

Transferability of untargeted authentication tools: a challenge

As previously mentioned, targeted methods are recognized for being robust and straightforward to transfer due to their adherence to well-established validation procedures, which are essential for any official method [45]. This is the main reason why current control methods rely on targeted approaches. In this context, recent research aimed at validating a targeted method based on VOCs by GC-MS for quality and authenticity assessment of olive oils [24]. Contrarily, untargeted approaches hinder reproducibility among operators and instruments, and validation procedures are still unclear [34]. Some authors proposed method validation strategies for untargeted metabolomic analysis [46] by adapting the target validation procedure to the detected chromatographic peaks in quality control samples. The main challenge in validating untargeted methods emerges in the context of fingerprinting methods within classification models, in which the raw analytical signal is considered rather than selecting specific chromatographic peaks. On top of that, when untargeted methods are based on VOCs by GC-MS, additional challenges may arise due to issues inherent to the analytical technique or the characteristics of the VOCs themselves, which can further complicate the transferability of authentication models. For instance, chromatographic fingerprints might vary because of GC column or SPME fiber brand and shelf-life. As Riedl et al. suggested [47], system challenge validations are needed to ensure the long-term stability of models, including the exchange of measurement data between laboratories. A preliminary in-house validation of fingerprinting for virgin olive oil has yielded promising results [36], but significant work remains to be done to successfully advance toward interlaboratory validations.

Moreover, authentication models should be regularly updated, including samples from new batches [47,48]. Continuous statistical modeling strategies have been proposed for some food products using spectroscopic methods [49], but more research is needed to extrapolate these approaches to GC-MS methods and to define validation protocols for untargeted methods to become reference methods. In the meantime, untargeted authentication tools built with in-house databases are promising as guidance for official inspections and conformity checks by the control bodies. In fact, EU member states shall ensure that conformity checks are performed selectively based on a risk analysis, where the untargeted screening tools could easily be included.

Conclusions

The analysis of volatile metabolome using GC-MS in the context of food fraud detection offers a promising tool for ensuring the authenticity and quality of food products (Figure 3). Untargeted profiling and fingerprinting emerge as the most comprehensive approaches for understanding food volatilome, showing significant potential as markers for both sensory quality assessment and authentication. Conversely, targeted VOC analysis represents a more readily transferable approach, with higher likelihood of application in official control procedures in the near future. Ongoing research is crucial to fully unlock the potential of these markers and improve the transferability of the methods.

Data Availability

No data were used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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