



A review of fruit juice authenticity assessments: Targeted and untargeted analyses

Lei Xu, Zhenzhen Xu & Xiaojun Liao

To cite this article: Lei Xu, Zhenzhen Xu & Xiaojun Liao (2021): A review of fruit juice authenticity assessments: Targeted and untargeted analyses, Critical Reviews in Food Science and Nutrition, DOI: [10.1080/10408398.2021.1895713](https://doi.org/10.1080/10408398.2021.1895713)

To link to this article: <https://doi.org/10.1080/10408398.2021.1895713>



Published online: 08 Mar 2021.



Submit your article to this journal [↗](#)



Article views: 171



View related articles [↗](#)




View Crossmark data [↗](#)

REVIEW



A review of fruit juice authenticity assessments: Targeted and untargeted analyses

Lei Xu^{a,b,c}, Zhenzhen Xu^a , and Xiaojun Liao^{b,c}

^aInstitute of Quality Standard & Testing Technology for Agro-Products, Key Laboratory of Agro-food Safety and Quality, Ministry of Agriculture and Rural Affairs, Chinese Academy of Agricultural Sciences, Beijing, China; ^bCollege of Food Science and Nutritional Engineering, China Agricultural University, Beijing, China; ^cBeijing Key Laboratory for Food Nonthermal Processing, Key Lab of Fruit and Vegetable Processing, Ministry of Agriculture and Rural Affairs, Beijing, China

ABSTRACT

Fruit juices are becoming more and more popular in the whole world. However, the increasing fruit juice fraud cases are undermining the healthy development of fruit juice industry. Fruit juice authenticity represents an important food quality and safety parameter. Many techniques have been applied in fruit juices authenticity assessment. The purpose of this review is to provide a research overview of the targeted and untargeted analyses of fruit authentication, and a method selection guide for fruit juice authenticity assessment. Targeted markers, such as stable isotopes, phenolics, carbohydrates, organic acids, volatile components, DNAs, amino acids and proteins, as well as carotenoids, will be discussed. And untargeted techniques, including liquid/gas chromatography-mass spectrometer, nuclear magnetic resonance, infrared spectroscopy, inductively-coupled plasma-mass spectrometry/optical emission spectrometer, fluorescence spectra, electronic sensors and others, will be reviewed. The emerging untargeted for novel targeted marker analysis will be also summarized.

KEYWORDS

Authenticity; fraud; fruit juices; untargeted for targeted analysis

1. Introduction

Fruit juice is the unfermented but fermentable liquid obtained from the edible part of sound, appropriately mature and fresh fruit or of fruit maintained in sound condition by suitable means including post-harvest surface treatments applied in accordance with the applicable provisions of the Codex Alimentarius Commission (2005). It is consumed worldwide, not only for their flavor and taste, but also due to their beneficial health effects (Zielinski et al. 2014). Its apparent consumption is expected to amount to 36,809.8 million liters by 2023 worldwide (Statista 2020). Many studies have suggested the effect of fruit juice components on human, such as preventing chronic inflammatory diseases, some cancers, cardiovascular diseases, as well as antimicrobial and anti-cariogenic effects (de Pascual-Teresa and Sanchez-Ballesta 2008; Diaz-Garcia et al. 2013; Pan, Lai, and Ho 2010).

According to the Global Food Safety Initiative, food fraud is an action "intentionally causing a mismatch between food product claims and actual food product characteristics, either by deliberately making claims known to be false or by deliberately omitting to make claims that should have been made" (Morin and Lees 2018). It consists of adulteration (substitution, dilution, unapproved enhancement and concealment), gray market, counterfeit and mislabeling. Fruit juice is a type of food commodity, which is often targeted

for fraud (Moore, Spink, and Lipp 2012), because it can be easily manipulated during processing (Jandrić and Cannavan 2017). Economically motivated adulteration (EMA) is a subset of food fraud, and has a potential for financial gain, and indeed undermines the rights and interests of consumers (Asadpoor, Ansarin, and Nemati 2014; Everstine, Spink, and Kennedy 2013). EMA of fruit juices from simple dilution with water/substitution of cheap ingredients (sugar, organic acid, artificial sweetener/flavor, colorant essence and other unknown adulterants) to sophisticated methods such as addition of by-products (peel extract or pulp wash) or less expensive juice to expensive juice (from concentrate (FC) juices to not from concentrate (NFC) juices, not organic juices to organic fruit juices) may be relatively common, and difficult to detect, depending upon the type of adulteration (Jandrić and Cannavan 2017).

The authenticity of fruit juice is the maintenance of its essential physical, chemical, organoleptical and nutritional characteristics of the fruit(s) from which it comes from (CODEX STAN 247, 2005). Food authenticity verification is important for food safety and has become more important due to globalization (Asadpoor, Ansarin, and Nemati 2014; Everstine, Spink, and Kennedy 2013; Koda et al. 2012). Currently, the published paper of fruit juice authenticity could be divided into two categories in our opinion, targeted and untargeted analyses. Targeted analysis focuses on the

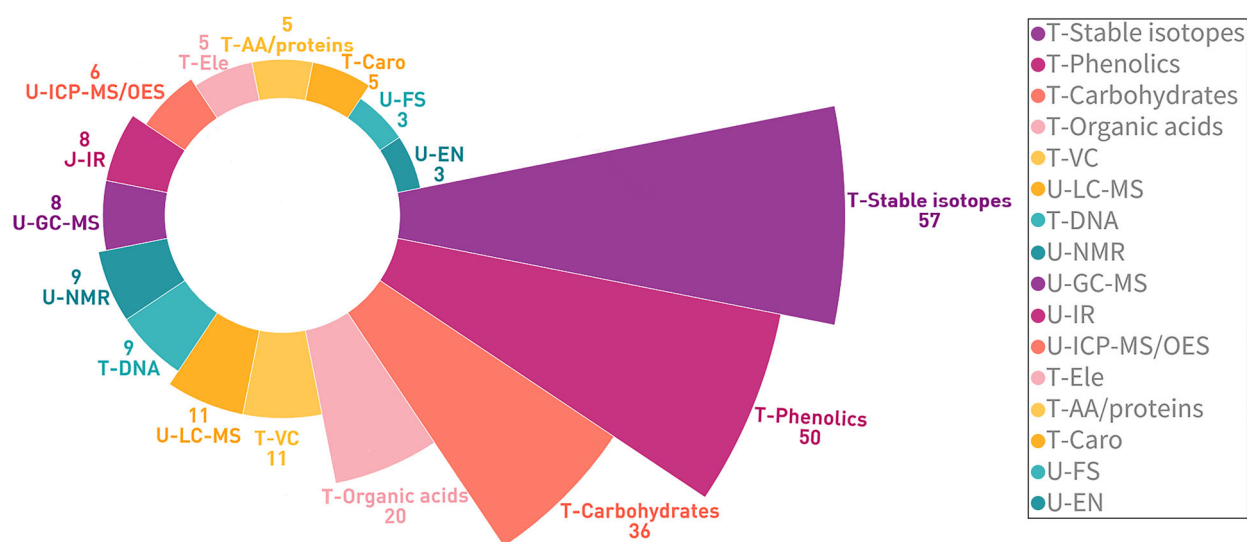
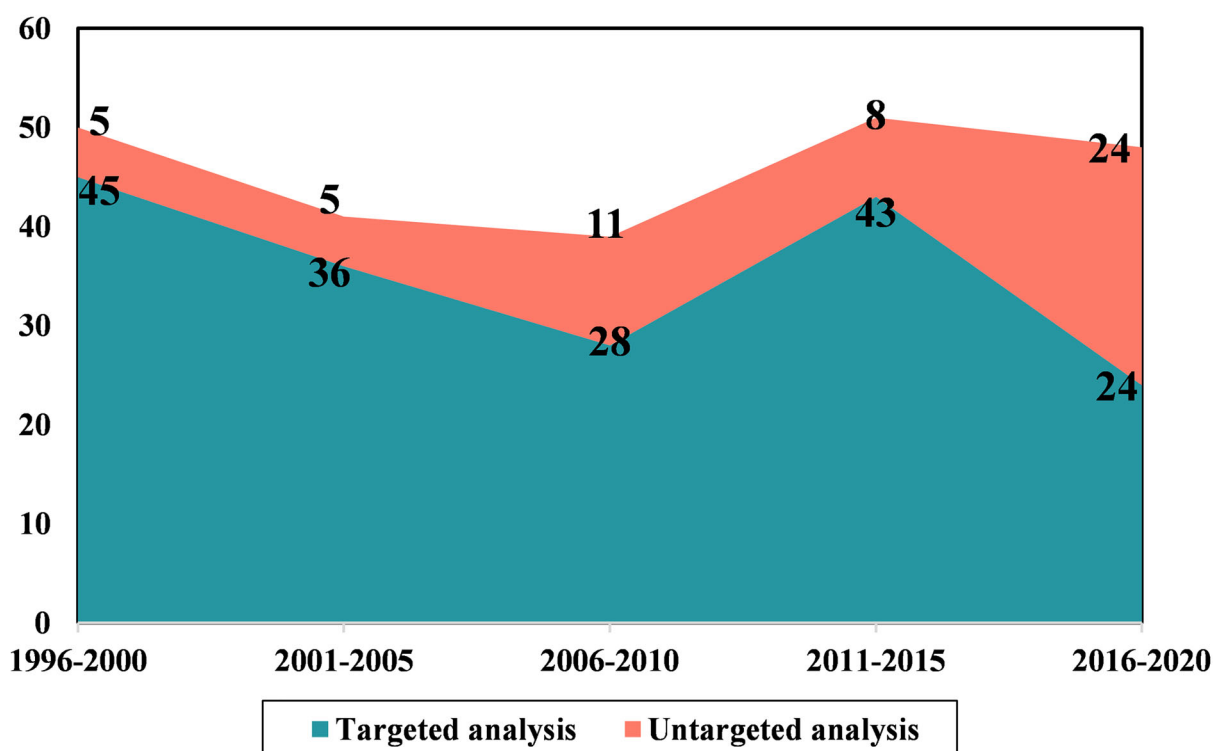


Figure 1. Statistics of the papers about fruit juice authenticity from 1996 to 2020 (T, Targeted; U, Untargeted; VC, Volatile components; Ele, Elements; AA, Amino acids; Caro, Carotenoids; FS, Fluorescence spectra; EN, Electronic nose).

identification and quantification of specific or characteristic compounds of fruit juices to test authenticity. On the other hand, untargeted analysis was used to investigate the “chemical fingerprint” or the general chemical profile of the samples based on large datasets (Spraul et al. 2009; Stander, Kühn, and Hiten 2013). So far, a detailed summarization of the targeted and untargeted authenticity assessments of fruit juices is not available yet. The main purpose of this review is to give a comprehensive summarization and discussion about the targeted and untargeted analyses of fruit juice

authenticity. Additionally, the future challenges and trends are also proposed.

2. Overview of the research status

We analyzed the 434 published paper from Web of Science searched by key words of “fruit juice authenticity.” After removing the irrelevant papers, the results were shown in Figure 1. There is a decline in paper number from 2001 to

Table 1. The targeted characteristic markers for common fruit juices authentication.

Fruit juice types	Targeted characteristic markers	References
Apple	Phlorizin, phloretin xyloglucoside, quercetin 3-O-rhamnoside, fumaric acid, quinic acid	Hilt et al. 2003; Fernandez de Simon et al. 1992; Lee and Wrolstad 1988; Shui and Leong 2002; Singhal, Kulkarni, and Dinanath 1997
Pear	Isorhamnetin-3-glucoside, arbutin	Schieber, Keller, and Carle 2001; Hofsommer and Koswig 1999
Peach	Myricetin, Lhcb2 (the chlorophyll a/b-binding protein)	Fernandez de Simon et al. 1992; Shang et al. 2014
Orange	Iso-citric acid, citrate/isocitrate ratio, chloroplast <i>trnT-trnL</i> intergenic spacer	Ježek and Suhaj 2001; Saavedra, Rupérez, and Barbas 2001; Mooney, Chappell, and Knight 2006
Mandarin	Chloroplast <i>trnT-trnL</i> intergenic spacer, <i>trnL-trnF</i> intergenic region, 314 position of intron belongs to chloroplast <i>trnL</i> gene	Mooney, Chappell, and Knight 2006; Aldeguer et al. 2014; Pardo 2015
Grape	Tartaric and quinic acids	Ehling and Cole 2011
Pomegranate	Ellagitannins	Borges and Crozier 2012
Pineapple	S-sinapyl-L-cysteine, N-γ-L-glutamyl-S-sinapyl-L-cysteine and S-sinapyl glutathione	Wen and Wrolstad 2002
Strawberry	Pelargonidin 3-glucoside, Serine, valine, methionine, aspartic acid	Obón, Díaz-García, and Castellar 2011; Stój and Targoński 2006
Red raspberry	Cyanidin 3-sophoroside, pelargonidin 3-sophoroside	Obón, Díaz-García, and Castellar 2011
Sour cherry	Cyanidin 3-glucosyl-rutinoside	Obón, Díaz-García, and Castellar 2011
Blueberry	Delphinidin 3-arabinoside	Obón, Díaz-García, and Castellar 2011
Black currant	Delphinidin 3-rutinoside	Obón, Díaz-García, and Castellar 2011
Red currant	Aspartic acid and serine	Stój and Targoński 2006
Black grape	Peonidin 3-glucoside and malvidin 3-glucoside	Obón, Díaz-García, and Castellar 2011
Grapefruit	Naringenin-7-O-neohesperidoside, naringenin-7-O-neohesperidoside-4'-O-glucose, naringenin-O-hexosylhexoside, hesperetin-7-O-neohesperidoside, Naringenin-O-rhamnosylmalonylhexoside, isosakuranetin-7-O-neohesperidoside, hesperetin-7-O-rutinoside, apigenin-6-C-hexoside-O-hexoside, apigenin-7-O-neohesperidoside, scopoletin-O-hexoside	Abad-García et al. 2014
Lemon	luteolin-7-O-rutinoside, eriodictyol-7-O-rutinoside-4'-O-glucoside, Eriodictyol-7-O-rutinoside, diosmetin-6,8-di-C-glucoside, diosmetin-8-C-glucoside, diosmetin-6-C-glucoside and diosmetin-6,8-di-C-hexosideacylhexoside	Abad-García et al. 2014
Papaya	<i>papain</i> (an archetypical member of a family of endopeptidase and cysteine proteinase)	Xu et al. 2008

2010, but a growth after 2011–2015, indicating the increasing attention of fruit juice authenticity.

These compounds used as specific or characteristic markers in targeted analysis include stable isotopes, phenolics, carbohydrates, organic acids, volatile components, DNAs, amino acids and proteins, as well as carotenoids and others. More specifically, stable isotopes, phenolics, carbohydrates and organic acids were widely used as the target objects in targeted analysis. Some of these targeted characteristic markers for common fruit juice detection were shown in Table 1. Numerous chemicals, physical and biochemical analysis techniques, such as liquid chromatography (LC), gas chromatography (GC), mass spectrometer (MS), nuclear magnetic resonance (NMR) and PCR have been proposed to use for the targeted analysis.

Obviously, targeted analysis is the dominating method used for fruit juice authenticity so far. However, there is an emerging trend of untargeted analysis combining with chemometrics for fruit juice authenticity assessment. Techniques like LC-MS, NMR, GC-MS, infrared spectroscopy (IR), inductively-coupled plasma-mass spectrometry/optical emission spectrometer (ICP-MS/OES), fluorescence spectra (FS) and electronic sensor (EN) are usually used for the untargeted analysis. Among them, LC-MS, NMR and GC-MS are three techniques usually used for the authenticity assessment which are usually based on the metabolomics profile analysis (Dona et al. 2016; Wiklund et al. 2008).

To process and interpret complex data obtained by untargeted analysis, advanced data mining/data processing algorithms and multivariate chemometric tools are needed (Vaclavik et al. 2012). First, principal component analysis (PCA) represents the most frequently employed method for initial exploration of data internal structure and sample clustering. In the next step, supervised pattern recognition methods, such as linear discriminant analysis (LDA), partial least squares discriminant analysis (PLS-DA), soft independent modeling by class analogy (SIMCA), support vector machine, and artificial neural networks are used for construction of classification and prediction models (Berrueta, Alonso-Salces, and Héberger 2007).

3. Targeted analysis

3.1. Stable isotopes

Stable isotopes are applicable for food authentication, because their ratios change with the climatic conditions, geographical origin, soil pedology and geology of the locations of food ingredients origin, evaporation intensity of the fruiter. It is difficult to circumvent as changing the isotopic ratios is not economically viable (Bong et al. 2008; Kelly et al. 2003). Isotope ratios of C, H, O, S, N, Si, and Sr are usually used.

As a primary indication, H and O isotopic data in foods is usually linked to the water from the source region which have geographical variability, N and C isotopes are related to the climate and the agricultural practices, and S isotopes are affected by geology, volcanism, distance from the sea, and certain anthropogenic effects (Drivelos and Georgiou 2012). Furthermore, changes of isotope ratios in authentic fruit juices may be also linked to season.

Depending on the origin of fruits, isotope ratios, especially heavy ones, become variable. These variations are due to kinetic or thermodynamic isotope effects and, therefore, reflect the circumstances under which physical or (bio-) chemical processes took place (Rummel et al. 2010). Camin et al. (2009) found the highbush blueberries from northern Italy showed significantly higher $\delta^{13}\text{C}$ values, and significantly lower $\delta^{15}\text{N}$ values than Romania and Poland. Isotope ratio of heavy elements (Sr, Pb) will come into use, if the results of light element isotopes remain ambiguous (Rummel et al. 2010). Regional variations of respective heavy isotope ratio are caused by radioactive decay of mother nuclides and radiogenic increase of daughter nuclides and are evolved during geologic processes. Isotopic signatures of the heavy elements in biogenous tissue are thus inherited from the geologic environment and therefore vary spatially depending on the regional geo-, litho- and pedological situation (Horn et al. 1993). Rummel et al. (2010) used isotope ratios of Sr and some light elements to determine and verify the geographical origin of orange juices from North and South-America, Africa and Europe successfully. Regional assignment of juice is most successful when single parameters are combined in a “multi-element approach,” especially heavy elements.

Simpkins et al. (1999) found $^{18}\text{O}/^{16}\text{O}$ ratios of orange juices ranged from a summer maximum of $> +15\text{‰}$ for oranges from inland regions to a winter minimum of $\sim +1\text{‰}$ for oranges grown in coastal areas in Australia. The effectiveness of isotope ratio analysis as a tool to detect juice authenticity could be improved by comparing isotope ratio data of samples to that of monthly authentic juice. But maybe not all isotope ratios are related to season. No significant seasonal variations in C isotope ratio were observed during their study of Australian orange juices (Antolovich, Li, and Robards 2001).

Isotope ratio also could determine the varieties/cultivars of raw materials for fruit juices. A research dated the stable isotope ratios of different varieties of soft fruits (strawberries, raspberries, blueberries, blackberries and currants), and the results showed a typical range for one or more isotopic parameters which can be used to verify the authenticity of the fruit composition declared on the label (Perini et al. 2018). Antolovich, Li, and Robards (2001) detected the C isotope ratio of Valencia and Navel juices, and established a decision level (-23.8 to -24.7 ppt for Valencia and -24.1 to -24.5 ppt for Navel) of these two cultivars of orange juices in Australia.

While, what else does also change the isotope ratios is exogenous addition, usually water, cheaper sugars and organic acids, to the fruit juices. The determination of the

^{13}C content of individual sugars enable a determination of the detection of added sugars in fruit juices. One study by González et al. (1999) showed that the $\delta^{13}\text{C}$ values of fructose, glucose, and sucrose allowed the detection of small adulterations by C3 sweeteners and of double adulterations by C3 and C4 sweeteners. Jamin et al. (2003) presented a procedure for the analysis of the $^{18}\text{O}/^{16}\text{O}$ of ethanol derived from the sugars of orange juice. A very strong correlation is observed between the isotopic deviations of ethanol and water, which is altered in the event of a water addition, even at a low level. A correlation between the C isotope ratios of sugars and malic acid has been observed, and the cutoff points concerning the difference of delta C values between them have been defined to improve the detection of sugar addition in apple juice. In the case of the addition of sugar from C4 plants (such as corn and cane), it has been demonstrated that the detection Limit can be as low as 5% whereas it is often higher than 10% while using the conventional carbon 13 method on the whole juice (Jamin, Gonzalez, Remaud, Naulet, Martin, et al. 1997). Similar result was achieved when dealing with adulteration of pineapple juice. The delta C values ratios of sugars, malic acid, and citric acid were studied, and the detection limit by sugar from C3 plants (such as beet) can be as low as 10% or even 5% (Jamin, Gonzalez, Remaud, Naulet, and Martin 1997).

Isotope ratio of C could also be used to detect the addition of organic acid as well. Guyon et al. (2014) determined the $\delta^{13}\text{C}$ of organic acids, as well as glucose and fructose, in lime and lemon juices from various geographical origins. These authentic samples allowed the definition of confidence domains which could detect the addition of C4 type organic acids or sugars.

No specific analytical method was able to differentiate between sugars coming from C4-metabolism plants (cane, maize, etc.) and some crassulacean acid metabolism plants (e.g., pineapple, agave), because in both cases the isotope distributions of the overall $^{13}\text{C}/^{12}\text{C}$ and site-specific $^2\text{H}/^1\text{H}$ isotope ratios are very similar. Until the quantitative isotopic ^{13}C NMR measurements, a procedure for the analysis of the positional $^{13}\text{C}/^{12}\text{C}$ isotope ratios of ethanol derived from the sugar using (site-specific natural isotopic fractionation) SNIF-NMR method is presented (Thomas et al. 2010). Thomas et al. (2010) determined positional $^{13}\text{C}/^{12}\text{C}$ isotope ratios of ethanol derived from the sugars of pineapple, which demonstrates a unique ability to detect cane and maize sugar, with a detection limit of 15% of the total sugar.

Dual or triple isotopes ratios are a more accurate method to detect exogenous source materials. Gonzalez et al. (1998) developed a methodology combining the use of the C and H isotopes of citric acid to detect the addition of exogenous citric acid from either C3 or C4 origin, with sensitivity of detection of $\sim 15\text{--}30\%$. Kelly et al. (2003) determined C and H isotope ratios to identify the addition of low-cost commercial sugar sirups to juice. The procedure utilizes the derivative hexamethylenetetramine, produced through chemical transformation of a sugar degradation product and provides position-specific ^{13}C and ^2H ratios that relate to the parent sugar molecule. The differences between the $\delta^2\text{H}$ and

$\delta^{13}\text{C}$ values of authentic apple juices and commercial sugar sirups from beet and cane permit their addition to be reliably detected. Pupin et al. (1998) measured the standard value of C and H isotopes ratios of ethanol and O isotope ratio of water in authentic orange juices. The determination of sugar or water addition in orange juices could be evaluated by comparison against the mean ratios found in authentic orange juices.

The processing methods and storage of fruit juices may also affect the stable isotope ratios. Isotope ratios of H and O could be used to distinguish NFC fruit juice and juice obtained FC efficiently. The presence detection of FC orange juice in NFC ones could be improved 37% by combining $\delta^{18}\text{O}$ ratios of water and sugar when compared to the use of water alone (Houerou, Kelly, and Dennis 1999). Kolesnov et al. (2014) also measured the O isotope ratio of the pomegranate fruit juices in Azerbaijan, which varies from -4.50 to -0.43‰ . The intracellular water of fruits is found to be richer in ^{18}O isotope than with the ground water ($\delta^{18}\text{O} = -9.69$ to -8.93‰). While Magdas et al. (2014) investigated both the O and H isotope ratio values of fruit juice water in Romanian, and the results revealed that NFC juices have elevated $\delta^{18}\text{O}$ and $\delta^2\text{H}$ content of water as compared to water from FC products, made using tap water which is relatively depleted in heavy oxygen and hydrogen isotopes. Furthermore, it was also demonstrated that blending of single strength juice by adding concentrate can be revealed by comparing $^{87}\text{Sr}/^{86}\text{Sr}$ of soluble and insoluble components of the juices (Rummel et al. 2010). Small changes to isotope ratios can occur as a result of storage, but these are unlikely to be significant in the context of authenticity testing (Simpkins et al. 1999).

3.2. Phenolics

Phenolics, including phenolic acids, flavonoids, stilbenes, coumarins, lignans and tannins, are important constituents of fruit juice. These compounds show a wide range of antioxidant activity in vitro, and are thought to exert protective effects against major diseases such as cancer and cardiovascular diseases (Boudet 2007; Shahidi and Ambigaipalan 2015). For some fruit juices, characteristic phenolics have been successfully used to detect the adulteration in other fruit juices (Abad-García et al. 2014). Moreover, quantitative differences may occur depending on fruit variety, stages of maturity, environmental conditions during growth, storage conditions, postharvest treatments, the presence of the peel in fruit-based products and the extraction system (Abad-García et al. 2012). Processing methods can have also a large influence here. As some fruits have highly active enzymes with polyphenol oxidase activity which will reduce the levels of phenolics significantly during processing, such as pear juice and apple juice (Yi et al. 2012).

Phloridzin (phloretin 2'-O- β -D-glucoside) is a characteristic phenolic compound of apple, which is a dihydrochalcone glucoside phenolic compound representing more than 90% of the water-soluble phenolic compounds in apple (Dong et al. 2007; Fromm et al. 2012; Gosch, Halbwirth,

and Stich 2010; Schieber, Keller, and Carle 2001). Phloridzin is also found in more than thirty plant families, such as orange, purple grape, strawberry; however, apple has the highest (120 mg/L) amount comparing to other fruits (Dong et al. 2007; Fromm et al. 2012; Gosch, Halbwirth, and Stich 2010; Hilt et al. 2003; Spinelli et al. 2016). Many researches have proved the high amount of phloridzin indicate the presence of apple juice (Hilt et al. 2003). However, drawing a sharp line of the phloridzin content between adulterated or non-adulterated with apple juice may be difficult. In spite of phloridzin, phloretin xyloglucoside, which also exists in apple juice in a comparatively large amount, is not detectable in others (Hilt et al. 2003). Therefore, simultaneous detection of phloridzin and phloretin xylosylglucoside, especially at higher levels, is an indicator of fraudulent admixtures, while phloridzin solely at low amounts may be not (Hilt et al. 2003). Phloridzin, combining with sorbitol, has also been proved that could be the indicator to determine authentic purple grape juice tampered with apple juice, as purple grape juice contain phloridzin content below the quantification limit and sorbitol content under 173 mg/L (Spinelli et al. 2016). Nevertheless, a low level of sorbitol may be due to the microbiological reduction of glucose during storage or processing (Ballester-Tomas et al. 2017). In contrast to the indicator of apple juice, Schieber, Keller, and Carle (2001) compared the comparison of phenolics between apple and pear juices, and found that isorhamnetin-3-glucoside may be the indicator for detection of pear admixtures in apple products instead of arbutin, which was used to be regarded as a characteristic marker for pear (Hofsommer and Koswig 1999). Furthermore, the mixture of peach and apple could be proved by high concentrations of phloridzin like in the apple and by the presence of myricetin like in the peach. There was also quercetin 3-O-rhamnoside, typical of apple but not in peach (Fernandez de Simon et al. 1992).

Sweet orange juice is often adulterated by tangerine, lemon or grapefruit, which are in the same *Citrus* category. Abad-García et al. (2014) compared the contents of polyphenols in 18 cultivars of sweet orange, tangerine, lemon and grapefruit juices, and found several markers that could distinguish grapefruit and lemon juices between them and other *Citrus* species. Grapefruit juice markers were naringenin-7-O-neohesperidoside, naringenin-7-O-neohesperidoside-4'-O-glucose, naringenin-O-hexosylhexoside, hesperetin-7-O-neohesperidoside, naringenin-O-rhamnosylmalonylhexoside, isosakuranetin-7-O-neohesperidoside, hesperetin-7-O-rutinoside, apigenin-6-C-hexoside-O-hexoside, apigenin-7-O-neohesperidoside and scopoletin-O-hexoside. Lemon juice markers were eriodictyol-7-O-rutinoside-4'-O-glucoside, eriodictyol-7-O-rutinoside, diosmetin-6,8-di-C-glucoside, diosmetin-8-C-glucoside, luteolin-7-O-rutinoside, diosmetin-6-C-glucoside and diosmetin-6,8-di-C-hexosideacylhexoside.

Among the berries, Obón, Díaz-García, and Castellar (2011) identified the anthocyanins and betacyanins in red fruits and every red fruit juice has one or more specific anthocyanins useful for its detection. Strawberry in a juice mixture can be detected by the presence of pelargonidin 3-

glucoside, red raspberry juice by cyanidin 3-sophoroside and pelargonidin 3-sophoroside, sour cherry by cyanidin 3-glucosyl-rutinoside. However, a mixture of those fruits may cause difficulties for its identification. Detection of pelargonidin 3-sophoroside indicates red raspberry presence, and blueberry is characterized by the presence of delphinidin 3-arabinoside. Blackcurrant is unambiguously characterized by the presence of delphinidin 3-rutinoside, black grape by peonidin 3-glucoside and malvidin 3-glucoside, and purple carrot by cyanidin 3-xyloxyl-galactoside-ferulic. Purple prickly pear is characterized by the presence of betanin. However, when using anthocyanins and betacyanins as targeted markers, their oxygen stability must be taken into consideration.

The phenolic composition of pomegranate is both complex and unique (Faria and Calhau 2011; Gil et al. 2000). Borges and Crozier (2012) compared the polyphenol profiles of red wine, pomegranate products (juices and beverages), with the latter being characterized by the presence of ellagitannins, and the former by flavan-3-ols monomers, procyanidin dimers and trimers. Moreover, the commercial 100% pomegranate juices with flavan-3-ol monomers, procyanidin dimers and trimers were found, which were not usually detected in pure pomegranate juices, indicating the adulteration of red wine (Borges and Crozier 2012). Twohig et al. (2011) found that chlorogenic acid was shown to be absent from authentic pomegranate juice, but identified in adulterated pomegranate juice. It may have the potential to provide an indication of adulteration. But Poyrazoğlu, Gökmen, and Artık (2002) reported the presence of chlorogenic acid in 13 different pomegranate varieties from four growing regions in Turkey. More qualitative and quantitative analyses of chlorogenic acid in pomegranate juice still need to be done.

Three main phenolic substances, S-sinapyl-L-cysteine, N- γ -L-glutamyl-S-sinapyl-L-cysteine and S-sinapyl glutathione, of authentic pineapple juices are unique in pineapple juice, and they could serve as characteristic markers for pineapple juice (Wen and Wrolstad 2002).

The addition of the peel wash in juices also affects the phenolics profile, as well as the juice features. Phlorin (3,5-dihydroxyphenyl β -D-glucopyranoside) was isolated from orange fruits as an orange peel marker (Louche, Gaydou, and Lesage 1998). Fischer et al. (2013) determined the monomeric phenolic and lignan profiles of pomegranate peels, mesocarp, seeds and juices obtained from isolated arils as well as from entire pomegranate fruits. Ellagitannins were found to be the predominant phenolics in all samples except in isolated arils juices.

Phenolic acids and catechins are important phenolic compounds in fruit juices, but they may not be the targeted markers to detect adulteration of fruit juices. Obón, Díaz-García, and Castellar (2011) determined the phenolic acids and catechins profiles of 8 fruits and 1 vegetable juice, but there were no specific compounds to distinguish each one.

The information above will be useful for evaluation of juice authenticity, but more profile analyses of different fruit juices are needed for the further assessment. And the effect of native polyphenol oxidases will also affect their usefulness

significantly, which must be taken into account (Yi et al. 2012).

3.3. Carbohydrates

Due to the high carbohydrate content of most fruit juices (>95% of the total soluble solids), a common EMA is the addition of readily available less expensive sweeteners along with water (Willems and Low 2014). Usually, sucrose (from cane or beet), invert sugar (total invert sugar (TIS) and medium invert sugar (MIS)), high-fructose sirups (HFS), hydrolyzed inulin sirup (HIS) and starch hydrolysates were used. When it comes to these issues, accurate knowledge of the carbohydrate profile, contents and their ratios could be a useful tool to determine fruit juice authenticity (Nikolaou et al. 2017). The principle to detect the adulteration of commercial sweeteners is the presence of these specific trace markers, which are not present in fruit juices normally, and are formed during the production of sweeteners by acid/enzymatic hydrolysis or isomerization. Thus, if these markers (could be known compounds or unknown peaks) are detected in fruit juices, it can be concluded the adulteration of corresponding commercial sweeteners (Stöber et al. 1998).

Direct addition of sucrose is relatively easy to detect. The addition of sucrose changed the approximately equimolar ratio of major orange carbohydrates, increasing the peak area of sucrose by 70% detected by capillary zone electrophoresis (Ídková and Chmelík 2001).

Originally, to detect the undeclared addition of HFS to pineapple juice (Low, Brause, and Wilhelmsen 1994), a procedure based on capillary gas chromatography (CGC) was developed (Low 1996). Later, it was extended as a procedure for both TIS and HFS detection in apple and orange juices based on the presence of fingerprint oligosaccharides, whose retention times are 39.3 (IS1) and 39.9 min (IS2), respectively. These two peaks, corresponding to two by-products formed during sucrose inversion with the IS2 peak is always larger than the IS1 peak, were present in sweeteners, but were either not present or at very low concentration in the pure juice samples. These two peak intensities will increase with heat processing, but were still even in the heated pure juice. However, their ratio (IS2/IS1) in adulterated juices usually exceed 2. When it comes to MIS adulteration, these two peaks were also present, but significantly lower intensity. To lower the detection limit of these two peaks, an equilibrium method, consisting of a pre-equilibration of the sample with dry pyridine followed by the addition of trimethylsilylimidazole, was introduced. This method was successfully used to distinguish heated pure juice, intentionally adulterated (with TIS and MIS), and intentionally adulterated and then heated apple juice concentrates (Low et al. 1999). Willems and Low (2014) employed oligosaccharide profiling using CGC with flame ionization detection to detect the debasing with four commercial sweeteners, high-fructose corn sirup (HFCS 55 and 90), HIS and TIS. They found α -inulobiose and β -inulobiose could be the HIS markers, O- β -D-fructofuranosyl-(2 \rightarrow 6)-D-glucose and the

unidentified peak with 41 min retention time the TIS markers, and β -isomaltose the HFCS marker. Detection limits for the four commercial sweeteners ranged from 0.5 to 5.0% (v/v). Traces of oligosaccharides, which are not usually present in the sugar profiles of fruit juices, but present in starch hydrolysates, were evaluated as the target compounds. Ídková and Chmelík (2001) developed a fast method to detect the oligomeric starch hydrolysates in orange juices, by the presence of equidistant peaks (162 mass-to-charge units) which were typical of polymers, as well as the maltooligosaccharides of the starch hydrolysates, using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). Otherwise, anion-exchange HPLC with pulsed amperometric detection was used to analyze the carbohydrate profile of fruit juices adulterated with beet MIS. Fingerprint oligosaccharides (either present in beet sugar or formed during sucrose hydrolysis for beet MIS manufacture) that were in either low concentration or non-existent from pure orange juices were discovered. With their help, detection of 5% beet MIS in orange juice was possible (Swallow, Low, and Petrus 2020).

Sugar contents combining with other parameters, such as acidity, organic acids and cations contents, could also be effective to detect the adulteration. Six cations (lithium, sodium, ammonium, potassium, magnesium and calcium) and four carbohydrates (fructose, glucose, saccharose and maltose) have been used to discriminate sweetened and non-sweetened apple and orange juices (Muntean 2010). Sorbitol and some phenolic compounds, combining with their saccharide profile, were well suited as a quick screening targets for the adulteration of main fruit juices consumed (Stander, Kühn, and Hiten 2013). Combining with the organic acid contents and physicochemical parameters (including acidity, pH, electrical conductivity and total dissolved solids), sugar contents analysis could determine geographical origin also confirmed by Nikolaou et al. (2017) with fresh Greek orange juice according to geographical origin, the results showed an overall correct prediction rate to 82.0%.

3.4. Organic acids

Organic acids are widely distributed in fruits, and used extensively as food acidulants in the manufacture of beverages and fruit drinks. The contents of organic acids in fruit juices influence not only their flavor but also their stability, nutrition, acceptability and quality keeping (Shui and Leong 2002; Türkyilmaz 2013). The differences in organic acids can be used as targets for authentication (Saavedra, García, and Barbas 2000).

The most common organic acids in fruits are citric, malic, tartaric and succinic acids (Karadeniz 2004; Türkyilmaz 2013). Methods to compare the major acids have been developed (Navarro-Pascual-Ahuir et al. 2015; Saavedra, García, and Barbas 2000). However, this is of limited value in most authentication cases, because it is easy to add synthetic organic acids to make the adulterated juice consistent with the pure juice (Ježek and Suhaj 2001;

Saavedra, García, and Barbas 2000). Analysis of some minor acids with lower variability could be a more powerful technique, because it is not economically feasible to adjust the levels of all acid components (Kvasnička et al. 2002; Saavedra, Rupérez, and Barbas 2001).

The lower content of iso-citric acid in orange juices may be due to dilution with some additive solutions, or juices made from orange sirups/powdered drinks, which contain only a small proportion of natural orange (Ježek and Suhaj 2001). Fumaric acid is also an indicator of apple juice quality and authenticity. Fumaric acid content varies from 0 to 1.7 mg/L in freshly prepared clarified apple juices (Lee and Wrolstad 1988), increases slightly during heat processing (such as evaporation, pasteurization and sterilization) because of the malic acid dehydration (Shui and Leong 2002). Fumaric acid contents in well-prepared authentic and fresh apple juices normally do not exceed 3 mg/L. It could also indicate the microbial spoilage (Shui and Leong 2002), processing of decayed fruits, or addition of synthetic malic acid, which contains fumaric acid as a minor contaminant (Singhal, Kulkarni, and Dinanath 1997).

The presence of tartaric and quinic acids in pomegranate juice was confirmed at concentrations of 1–5 and ~1 mg/L using a specialized LC-MS method (Ehling and Cole 2011). The concentrations are much lower than those resulting from the adulteration with grape juice or apple juice, respectively, at the 5% level. Tartaric acid is considered as an indicator of grape juice addition to a more expensive juice.

However, there were conflicting reports on the presence of tartaric acid and quinic acid in pomegranate juice as the potential indicators of adulteration with grape juice (Fischerzorn and Ara 2007; Melgarejo, Salazar, and Artés 2000; Zhang et al. 2009). The reason may be the differences in fruit provenance, juice processing or analysis method.

Saavedra, Rupérez, and Barbas (2001) determined the contents of citric, iso-citric, tartaric and malic acids in orange juices, and found that citrate/isocitrate ratio could be a more reliable parameter to establish regulation because of the lowest relative standard deviation comparing to ratios of citrate/malate and malate/isocitrate. A range of citrate/isocitrate ratio (113 with RSD = 10%) to identify the authenticity of oranges juice was established. Through further researches, the use of the minor organic acid ratios in specific juices may be a more sensitive indicator.

3.5. Volatile components

Volatile components, including alcohols, aldehydes, esters, ketones, hydrocarbons, and certain terpenes, are reported to contribute to the pleasant aroma of fruit juices (Ruiz Del Castillo, Caja, Blanch, et al. 2003), which could serve as good targets of freshness, quality and authenticity (Socaci et al. 2013).

Over the past few years, the detection of chiral volatile components has been developed as a valuable tool in the fraud detection of fruit juices. When dealing with enantiomeric components, the sample preparation technique is

crucial to the result, since harsh experimental conditions can bring about racemization. A comparison between steam distillation-solvent extraction and solid-phase micro-extraction revealed the latter to be more reliable for stereochemical studies (Ruiz Del Castillo, Caja, Blanch, et al. 2003).

König and Schreier (1999) argued that apple juices with (S):(R) ratio of ethyl-2-methylbutanoate > 99.1% were authentic. They also found ethyl 3-methylbutanoate and 3-methylbutyl acetate were not present in authentic samples. When it comes to detection of exogenous flavor addition, chiral compounds work well (Caja et al. 2004). Ruiz Del Castillo, Caja, and Herraiz (2003) determined the enantiomeric distribution of chiral terpenes, mainly limonene, linalool, and R-terpineol, which exhibited a considerable variation among samples. These compounds occur in nature with enantiomeric distributions of 100, 100, and 80%, respectively, the (+)-enantiomer being the predominant isomer in all cases. Any alteration in these values could be attributable to the addition of aromas. And Hansen, Frandsen, and Fromberg (2016) found juices contained almost only R- (E)- α - ionone supporting the content of natural raspberry aroma, and that R- α -ionone and S- α -ionone were detected at an enantiomer ratio of 50% indicating the use of synthetic aroma in the products. Bocharova et al. (2017) found that the presences of d-limonene and benzoic acid in orange juices also indicated the presence of added flavors.

The volatile components could help to determine the authenticity origins of juice products. Enantiomeric ratio of terpinen-4-ol and β -citronellol could be indicators of the geographical origins (Spain, Florida and Brazil) of orange juices, as the enantiomeric excesses, calculated by (predominant enantiomer – minor enantiomer)/(predominant enantiomer + minor enantiomer) \times 100%, were terpinen-4-ol: (+)32.0%, (–)17.4%, (+)63.2% and β -citronellol: 78.9%, 28.5%, 3.2% in orange juices from Spain, Florida and Brazil, respectively (Ruiz Del Castillo, Caja, Blanch, et al. 2003).

The contents of volatile component could help to discriminate the fruit juices with different processing methods. Some reports (Moshonas and Shaw 1994; Nisperos-Carriedo and Shaw 1990; Shaw, Buslig, and Moshonas 1993) determined the extensive volatile components threshold values, and compared the volatile flavor components of fresh and processed juices of pineapple and orange. They found unpasteurized and pasteurized NFC juices did not show marked changes when compared to fresh juice. In contrast, pasteurized FC juices from concentrate showed decreases in acetaldehyde, methyl acetate, methyl butyrate and ethyl butyrate, with increases in decanal, octanal and linalool. However, Caution must be needed here as many FC juices will have their aromas restored to make up for losses during concentration. And the introduction of aromas and flavors are allowed to restore the level of these components up to the normal level attained in the same kind of fruit (CODEX STAN 247, 2005).

Amounts of volatile components could also distinguish the cultivars of juice materials. Allegrone, Belliardo, and Cabella (2006) compared the volatile component contents of

fresh lemon juices from four Italian cultivars, and observed significant differences (Verdello Siracusano lemon juice with 50.28 mg/L volatile compounds, followed by Interdonato with 8.39 mg/L, Primo Fiore Capo d'Orlando with 5.75 mg/L, and Femminello Siracusano with 2.62 mg/L). Furthermore, for orange juices produced with or without additional food flavors, the intensity of odor was found to be 2 times higher or 1.5–2.5 times lower than that of freshly squeezed juice, respectively (Bocharova et al. 2017).

3.6. DNAs

Qualitative and quantitative PCR assays using species-specific genes can be applied to determine the food source, and confirm the relative content of certain species in a complex food matrix, as well as juice adulteration detection. A number of species-specific genes have been identified to detect the presence of species-specific foods (Ding et al. 2004; Liu et al. 2012; Yang et al. 2005).

As for fruit juices, Xu et al. (2008) and Shang et al. (2014) selected and validated the *papain* (an archetypical member of a family of endopeptidase and cysteine proteinase) and *Lhcb2* (the chlorophyll a/b-binding protein) as the species-specific genes for the papaya and peach, respectively. They confirmed the unique and low copies (one or two) of the genes by PCR and southern blot. In real-time quantitative PCR analysis, the detection limit was as low as 10 pg and 5 pg of DNA. However, the major hindrances of species-specific genes approach are the availability of unique, reliable, reproducible and discriminant marker genes. The Sequence Characterized Amplified Regions (SCAR) markers may allow to overcome the limitation owing to high sample throughput, short sample preparation, unique identification, good interlaboratory replicability and low operating costs (Marieschi et al. 2016; Marieschi, Torelli, and Bruni 2012). A method based on SCAR markers was developed from RAPD specific for ten common bulking agents used for economically motivated adulteration of pomegranate. The method enabled the unequivocal detection of low amounts of contaminants up to 1% and was successfully tested on different commercial samples (Marieschi et al. 2016).

When dealing with closely related species, such as orange and mandarin, which have been subjected to extensive cross-breeding, similar genetic markers may be shared between them. Multilocus markers are difficult to resolve from complex mixtures (Mooney, Chappell, and Knight 2006). To overcome these problems, some methods have been applied. Mooney, Chappell, and Knight (2006) used PCR-based heteroduplex assay to detect the addition of mandarin juice in orange juice. PCR amplification of a fragment of the chloroplast *trnT-trnL* intergenic spacer derived from mixtures of DNA extracted from orange and mandarin juice resulted in heteroduplex formation. The heteroduplex resulted from the co-amplification of a fragment containing an 8 base-pair indel that distinguished mixtures of orange and mandarin juice from orange juice and mandarin juice alone. The heteroduplex assay was evaluated against authentic juices obtained from different citrus species and

confirmed that the marker was homogeneous within Citrus. The method also did well in quantitative and qualitative analysis. Then, Scott and Knight (2009) applied the laboratory-on-a-chip capillary electrophoresis (LOC) technology to the mandarin detection in orange juices.

The Chloroplast DNA has also been completely sequenced from a number of plants. Although in general chloroplast sequences are highly conserved, well-characterized variable regions still exist, which can provide polymorphic markers for species identification (Mooney, Chappell, and Knight 2006). Aldeguer et al. (2014) confirmed a single nucleotide polymorphism at the *trnL-trnF* intergenic region of the chloroplast chromosome for the identification of mandarin in orange juice. The method allowed a simple estimation of the ratio mandarin/orange in the juice samples, with a 5% detection limit of mandarin added in fresh orange juice. Pardo (2015) found a single nucleotide polymorphism at the 314 position of intron belongs to chloroplast *trnL* gene. They also used dual-probe real time PCR with precision of 100% and a lower limit of detection of 1% presence of mandarin in orange juice.

High resolution melting analysis (HRMA) is a technology based on the classical melt analysis of PCR fragments, it uses instrumentation improvements to measure the melting behavior and new saturating DNA dyes (Bosmali et al. 2012). It measures the rate of double stranded DNA dissociation to single stranded DNA with increasing temperature to discriminate different DNA sequences easily visualized throughout the melt curve (Reed and Wittwer 2004). HRMA has been applied to fruit juice authenticity using the DNA barcode *trnL*, allowing the discrimination of five species (orange, mango, peach, pear, and pineapple). The fragment used was around 500 bp long, the mixtures of different juices were discriminated completely (Faria et al. 2013). HRMA is also used on microsatellite fragments to have cultivar specific authenticity tests for processed sweet cherry products, and is proved to be a useful approach for identifying sweet cherry products made from specific cultivars (Ganopoulos, Argiriou, and Tsaftaris 2011). DNA barcoding technology was also used for identifying both known and unknown fruit species in small berry fruit (blue berry, red raspberry, cranberry, black raspberry, mulberry, kiwi fruit strawberry and blackcurrant) products successfully. The method established based on mini-barcodes of *rbcL* and *ITS* and a medium-barcode of *psbA-trnH* could detect 1% to 10% target species in mixed fruit juice (Wu, Li, et al. 2018).

Methods based on DNA are easy to optimize the experiment conditions, and suitable for some juice authenticity cases. But the content of DNA in fruit juices is relatively low and susceptible to thermal processing under acid conditions. Heat denaturation could accidentally have potential applications in identifying adulteration of thermal processed juice in freshly squeezed juices. Ng et al. (2006) found that when orange juices were heated to 80 °C for 30 s caused damage to DNA integrity, thus failing in amplification by primer 18S-ITSe, which gives a PCR product of 2081 bp, whereas primer 18S-ITSf, fragment length 2421 bp, could only be seen in heating conditions less stringent than 70 °C

for 15 s. Furthermore, during the clarification process of clarified juice, fruit pulp was removed, thus collection for DNA became difficult (Han et al. 2012).

3.7. Amino acids and proteins

Amino acids and proteins are important compounds, because they participate in many essential and well-known physiological processes (Asadpoor, Ansarin, and Nemati 2014; Gómez-Ariza, Villegas-Portero, and Bernal-Daza 2005; Sun 2008). They also affect the quality of juices including taste, aroma, and color (Fabiani et al. 2002).

Amino acids could also be feasible markers for determination of the authenticity of fruit juices, as many adulterations, such as simple dilution with water, addition of cheaper juices from other types of fruits, or addition of inexpensive amino acids, could change the amino acid profile.

The approaches for detecting all these frauds include the measurement of specific individual amino acid. Serine, valine and methionine can be the indicators of addition of strawberry juice to raspberry juice, aspartic acid and serine for addition of red currant juice to raspberry juice, aspartic and methionine for addition of strawberry juice to black currant juice (Stój and Targoński 2006). Gómez-Ariza, Villegas-Portero, and Bernal-Daza (2005) compared the twenty α -amino acids in fresh hand-squeezed and commercial orange juices, and found that the total content of amino acids, as well as the proline concentration, may indicate dilution with water or addition of sugar sirup. The addition of apple juice to orange juice can be detected by a reduction in the levels of aspartic acid and arginine. In general, determining the amount of amino acids and comparing with the standard values is an effective method for quality control. This can provide the regulatory agencies with a tool to assist in quality control.

The analysis of amino acids could also determine the origin of fruit juices. Aiming at differentiating the origin of orange juices coming from different areas, even from the neighboring regions (Sicily and Calabria), Licciardello et al. (2011) assessed and discussed the distribution of free amino acids of orange (blood and blonde varieties) juices. The total free amino acid content, as well as the level of proline, arginine, aspartic acid, asparagine, serine and glycine can be considered as markers of geographic origin, contributing to sharply discriminate blonde Sicilian orange varieties from Calabrian ones.

Proteins could be used as the target to determine the varieties of fruit juice materials. Hayasaka et al. (2001) had developed methods based on LC-MS and protein trap MS to determine the pathogenesis-related (PR) proteins in 19 different varieties of grape juice. Although the PR proteins are highly conserved, small consistent differences in molecular masses were noted when comparing with different varieties. With the contents of four different masses for PR-5 (thaumatin-like) proteins (range = 21,239–21,272 Da) and nine different masses of PR-3 (chitinases) proteins (range = 25,330–25,631 Da), and using statistical analysis, the method

developed could be used for varietal differentiation of grapes. The stable isotope profile of juice protein is also useful for variety and origin distinguish due to the lower metabolic turnover than metabolites (Jamin et al. 1998).

3.8. Carotenoids

Carotenoids are one of the main classes of natural pigments that have been investigated extensively, they also provide organoleptic and functional properties that are attractive to the consumer (Giuffrida et al. 2010).

Oranges are important source of carotenoids, and xanthophylls is the main carotenoid class found in citrus fruit (Murador et al. 2019). Some other carotenoids play a large role in citrus origin authenticity, such as phytofluene, which is lower from Belize than from Spain (0.5 vs. 1.8%), or ξ -carotene, which is higher in Valencia from Spain (4.9%) than in Valencia from Belize (1.8%). Mouly, Gaydou, and Corsetti (1999) had quantitated the major carotenoid pigment of Valencia pure orange juice from Belize and Spain. The total carotenoids considered were higher in Valencia juice from Spain (17.0 ± 5.0 mg/L) than in Valencia juice from Belize (4.8 ± 1.0 mg/L).

Among the carotenoid comparison of seven different orange juices and a commercial orange juice, special attention was given to the epoxycarotenoids components, whose relative proportions and compositions can be used to estimate the age and freshness of orange (Dugo et al. 2009). Some carotenoids can be found in either their free form or in fatty acid esterified form in the case of mono- and poly-hydroxylated xanthophylls. The study of carotenoid ester composition has been proposed to evaluate fruit products' authenticity. Giuffrida et al. (2010) studied the native (carotenoid esters and free carotenoids) carotenoids in orange juices from eight different varieties, and found some distinguish between varieties. These contributions clearly could be used to establish authenticity markers among orange varieties that could potentially be used to prevent adulteration.

3.9. Others

There are other physicochemical parameters, such as antioxidant activity, color and turbidity, combining with phenolics, carbohydrates, organic acids, which were used for fruit juice authenticity analysis (Gökmen et al. 2001; Subasi and Alpas 2017).

Measuring electrical impedance is a noninvasive and in real time method for fruit juice authentication. It was applied on orange juice dealing with water, sugars and citric acid detection successfully (Prusova et al. 2017). A conductometric method for the determination of diluted apple juices with water, as well as with ascorbic acid, was substantiated. It has been demonstrated that polarization curves of a platinum electrode in apple juice are useful for undeclared antioxidant determination, as a result of the movement of the polarization curve to the left, by 200 mV, when ascorbic acid was added. The criterion values range

from 0.030 to 0.034 S m^{-1} for juices of different apple varieties. It has been established that the volt-ampere method is useful for the investigation of undeclared addition of ascorbic acid (Bocharova et al. 2018).

A method using capillary isotachopheresis (ITP) was applied for the authenticity or adulteration of orange juices by determining the anionic profile. Special emphasis was placed on D-isocitric acid ITP determination as a reliable fruit juice authentication marker (Ježek and Suhaj 2001).

4. Untargeted analysis

Currently, because of the increasing complexity and uncertainty of fruit juice frauds, there is an emerging trend for the use of untargeted analyses combining with chemometrics for fruit juice authentication (Figure 1A).

4.1. LC-MS

In the recent years, MS hyphenated to chromatography, including LC and GC, is appearing as a less expensive and more sensitive alternative approach for fruit juice authentication. It is very powerful when modern analyzers are employed (Dunn and Ellis 2005). The wider range of separation mechanism in chromatography makes it more suitable to develop profile methods, and expand the applicability from medium to highly polar compounds (Diaz et al. 2014).

Some related profile work has been done to detect the fruit juice adulteration. The comprehensive metabolomic fingerprint of several fruit juices, from expensive (orange) to relatively low-priced (apple and grapefruit) juices were determined by LC-MS. The constructed LDA model was able to reliably detect 15% addition of low-priced juices to expensive juice (Vaclavik et al. 2012). Better results, which could differentiate authentic fruit juices and their adulterated mixtures down to 1% adulteration level, were achieved when dealing with pineapple, orange, grapefruit, apple, clementine and pomelo juices (Jandrić et al. 2014). Similar metabolomics approach was proved to distinguish pomegranate juice adulteration to a level down to 1% by apple and red grape juice (Dasenaki et al. 2019).

LC-MS based metabolomics was also used for the discrimination of variety and geographical origin. Diza et al. used it for authenticity identification of Spain Valencia oranges from foreign (Argentinean, Brazilian and South African) oranges with 100% accuracy by PLS-DA model (Diaz et al. 2014). To distinguish the different variety of fruit juices, LC-MS based metabolomics combining with PLS-DA and SIMCA achieved the results with 100% recognition ability obtained for citrus fruits/orange models. The detection limits tested by external data sets were 1% for adulterated with other fruit juices and 5% for dilution with water (Jandrić and Cannavan 2017). Further, to discriminate authentic and adulterated juices by the juices from the same category, Jandrić et al. (2017) also did the research for citrus juices determination. The results showed that with the help of PCA and SIMCA, the adulteration of citrus juices with

similar types of juices at very low levels (down to 1%) could be detected.

Juices from different cultivars also could be discriminated by LC-MS. PCA approaches of pear juice profiles from different cultivars (Alejandrina, Conference, and Blanquilla) could achieve satisfactory discrimination (Delpino-Rius et al. 2019). And the metabolomic profiles of juices and by-products, such as peels and trimmings are different. It was reported that the pineapple juices from pulp and those from peel could be distinguished based on metabolite profiles by LC-MS (Difonzo et al. 2019).

4.2. NMR

Traditionally, NMR has been perceived as a tool for structure verification, elucidation and purity analysis (Raman et al. 2010). However, driven by the need of the emerging field of metabolomics, NMR has been rapidly expanded into the quantitative compositional analysis and profile screening areas (Arana et al. 2015; Panarese et al. 2012). Although the latter employs chemometric to analyze the data from complex spectra, it is often possible to locate specific sections of the spectrum and to make reasonable assumptions about why one sample stands out from the rest (Cuny et al. 2007).

The difference results from variety and geographical origin could be detected by NMR profile. NMR fingerprint was used to detect the adulteration of orange, blood orange, mandarin, clementine, cravo or tangerine in lemon juices. Sinensetin higher than 0.015 mg/L in lemon juices was deduced. Lower concentrations indicate a carry-over and are not considered as adulteration (Lehnert, Schmidt, and Ara 2017). Vigneau and Thomas (2012) investigated NMR profile to discriminate orange juices adulteration of clementine juices successfully. Koda et al. (2012) used metabolic analysis with NMR to discriminate five different mango cultivars. It was found that arginine, histidine, phenylalanine, glutamine, shikimic acid, and trigonelline were important for the classification. Cicero et al. (2015) studied the main metabolites of from different origins (Interdonato Lemon of Messina and the Interdonato Turkish), and found that the former is richer in asparagine, fructose, glucose, malic acid and myo-inositol, the latter is richer in fatty acids, γ -aminobutyric acid, arginine, choline, isoleucine, leucine, lactic acid, methanol, proline, tryptophan and valine.

Processing conditions have also been shown to affect the NMR profiles. NMR coupled with chemometrics could detect the simple additions of sucrose, beet MIS, sodium benzoate easily. And the accuracy of classification reported could be 94% (Vogels et al. 1996). The undeclared off-line addition of pulp wash, which is paler, bitter, and regarded as a lower quality byproduct, is usually forbidden (CODEX STAN 247, 2005; Le Gall, Puaud, and Colquhoun 2001; Mauro et al. 2002). NMR could serve as a tool for pulp wash detection in fruit juice. Le Gall, Puaud, and Colquhoun (2001) used NMR as a tool for detection of pulp wash in orange juice. A model, which could give a 94% classification rate, was constructed, and they discovered that

dimethylproline could be used as an indicator for pulp wash addition.

Part of the NMR screening profile, such as carbohydrate, amino acid and primary metabolite profiles, could help with variety/cultivar discrimination. Cuny et al. (2007, 2008) located the specific sections (containing the flavonoid glycoside markers and another zone with sucrose, α -glucose and other components signals) when investigating the determination of adulteration of orange juice with grapefruit juice by NMR. Then, independent component analysis was applied on three different groups of selected regions and showed good results for both discrimination and interpretation of the signals, and up to 97.8% of the juices were attributed correctly. Combining with chemometric, amino acid profile of fruit juices could be a potential specific fingerprint discriminating fruit varieties from different genera (Botoran et al. 2019). And with the help of PCA, primary metabolites allowed satisfactory discrimination of pear cultivars including Alejandrina, Conference, and Blanquilla (Delpino-Rius et al. 2019).

Due to the reproducibility of NMR, it can be transferable between different instruments of the same field strength and different laboratories (Di Anibal, Ruisánchez, and Callao 2011; Spraul et al. 2013). Untargeted NMR screening approach features low cost per sample, and is highly competitive with conventional targeted fruit juice quality control methods (Spraul et al. 2009). In addition, the time required to carry out the NMR analysis was less than half the time of the standard chromatographic method (Cuny et al. 2007). Spraul et al. (2009) developed a fully automated system with respect to sample transfer, measurement, data analysis and reporting and is integrated on a NMR spectrometer. Multitude parameters related to juice quality and authenticity could be evaluated simultaneously from a single data set acquired within a few minutes.

4.3. GC-MS

A combination of the separation power of GC with the capabilities of the modern MS instruments makes it a better choice for the analysis of any type of complex chemical and biological samples (Hurtado-Fernandez et al. 2013). Unlike LC-MS, it was reported that no significant differences were found between the fingerprints of volatile profiles of whole fruits and juice samples, and the pretreatments could be simpler for GC-MS (Socaci et al. 2013). It could be used as routine method for fruit juice authenticity determination (Cagliero et al. 2012).

Adulteration could affect the volatile profile of fruit juices. Methods using HS- GC-MS to assess the authenticity of commercial Noni juices were developed, allowing differentiating between authentic and adulterated products by use of PCA. The method also allowed the undeclared addition of preservatives benzoic acid and sorbic acid to be detected (Lachenmeier et al. 2006).

The variety and geographical origin of raw material plays a crucial role in the quality and authenticity of fruit juices. GC-MS was utilized to illustrate the differences of volatile

compounds among juices, identify the novel markers, provide useful access to differentiate juices (Wu et al. 2017). For apple juices from varieties (Rijo, Verde, Ribeiro, and Azedo) and geographical origin (Prazeres and Santo da Serra (Madeira Island)), a discrimination method was established (Medina et al. 2019). A fast and efficient GC-MS method was developed on sea buckthorn juices from different varieties and geographical origins. PCA showed a good discrimination of samples from different origins, and samples from wild and cultivated berries (Socaci et al. 2013). In addition, model based the aroma profiles achieve 100% accuracy for orange and apple juices from Slovenian and foreign producers. Fruit juices and fruit nectars could also be discriminated (Kosir and Kolar 2010).

The contents of volatile aroma compounds in fruit juices vary after different processing conditions, GC-MS has the potential for discriminating fruit juices according to the processing methods. Effects of high hydrostatic pressure (HHP) and pasteurization on orange juice were investigated. Processing decreased the contents of most terpenes and esters and increased those of alcohols and aldehydes. The compounds d-carvone and β -terpineol could be used as novel markers of HHP-treated and pasteurized orange juice, respectively (Bi et al. 2020). Commercially available and freshly prepared citrus juices was also compared by GC-MS. Apparent tendencies could be determined. However, to be able to identify unambiguous tasks in authenticity, additional effort needs to be made to continuous measurements of authentic samples and update of the corresponding data bases (Medina et al. 2019).

4.4. IR

IR spectroscopy has gained the capability of rapidly obtaining reproducible biochemical patterns that would allow for the composition-based statistical classification, and could become an effective tool for fruit juice authentication. This nondestructive technique requires minimal, even no sample preparation and low sample volume, and is environmentally friendly. Nearly real-time measurement was made possible by immediate prediction with minimal operational cost (He, Rodriguez-Saona, and Giusti 2007).

One of the many forms of adulteration is dilution which can then be disguised with commercial sweetener solutions, or juices from other fruits or vegetables, which mimic the natural fruit sugars, and IR contained the information allowing for the discrimination and quantification of these kinds of adulteration (Ellis et al. 2016).

Fourier Transform (FT)-IR has been used to detect adulteration of apple juices by commercial sweeteners. With the help of PCA, k-nearest neighbors and PLSR, the prediction results achieved an overall correct classification rate of 96.5, 93.9, 92.2, and 82.4% for partially inverted cane sirup, beet sucrose, HFCS, and a synthetic solution of fructose, glucose, and sucrose, respectively (Kelly and Downey 2005). Some others commercial sweeteners could achieve detection limit of 9.5% for samples adulterated with HFCS (45% fructose and 55% glucose), 18.5% for samples adulterated with

SUGARS (60% fructose, 25% glucose, and 15% sucrose), and 17% for the combined (HFCS + SUGARS) adulterants by IR in apple juice. Discriminant PLS regression can determine authentic apple juice with an accuracy of 86–100% and adulterant apple juice with an accuracy of 91–100% (depending on the adulterant type and level of adulteration considered) (León, Daniel Kelly, and Downey 2005). The feasibility in mango juice was also proved. PLS-DA and PCA were used to classify the samples with or without added sugar. The detection limit for added sugar was 3% for samples with low natural total soluble solids, 5% for samples with natural total soluble solids more than 10% and 3.6% for commercial samples (Jha and Gunasekaran 2010).

FT-IR could also be used for the content prediction of sweetener adulteration in juice. With the help of PLSR, FT-IR could predict the addition contents of glucose, fructose or sucrose individually, even these three sugars at appropriate concentrations found in freshly prepared orange juice with excellent accuracy (with typical error of 1.7%) (Ellis et al. 2016).

Variation in the chemical composition attributed to variety and geographical origin, might be elucidated through spectral-based chemometric analysis. He, Rodriguez-Saona, and Giusti (2007) sorted commercial juices using attenuated total reflectance IR spectroscopy combining with SIMCA. Solid-phase extraction enriched phenol compounds and provided signature-like spectral information that substantially improved the modeling power over the whole juice or sugar-rich fraction models and allowed for the differentiation of juices with different origins. Zero percent misclassification was achieved by the phenol-rich fraction model. FT-IR was also used to a classify white grape juices into variety categories. A PLS-DA model constructed achieved a satisfactory result with 9.6% classification error level (Roussel et al. 2003).

4.5. ICP-MS/OES

Comparing to phytochemicals, which are more affected by random environmental changes, the multi-element contents in foods, including macro and microelements, clearly reflects the soil type and the environmental growing conditions. Thus, their contents could be the discriminative marker, and have been applied to develop methods for the juice authenticity determination (Benabdelkamel et al. 2012). Among the numerous techniques that exist for elemental analysis, ICP-MS/OES has been widely used as sensitive and economic methods to analyze a wide range of elements, even trace levels (Borges et al. 2016; Magdas, Dehelean, and Puscas 2012).

Multielement analysis has been used for the identification of juice geographical origins, discrimination of organic and conventional juices, and adulteration detection.

Benabdelkamel et al. (2012) determined the concentration of 26 elements in Clementine juice of Calabria in Algeria, Tunisia, and Spain, and used stepwise linear discriminant analysis (S-LDA) and SIMCA to build chemometric models, which could be able to protect the protected geographical indications (PGI) of Clementine from others. A cross-

validation procedure has shown very satisfactory values of prediction ability for both S-LDA and SIMCA (96.6% and 100% separately).

Borges et al. (2016) carried out the concentration determination of 24 elements in organic and conventional grape juices to classify them. The concentrations of 9 elements were found to be higher in organic versus ordinary samples, while Na and Va higher in ordinary versus organic samples. PCA and SIMCA models of the elemental fingerprints were readily able to discriminate organic from ordinary samples. Maione et al. (2016) also did a research about elements in organic and conventional grape juice. They found that the components of Na, Sn, P, K, Sm, and Nd are the most important variables in the differentiation of organic and conventional samples. The support vector machine model yielded an accuracy of 89.18%, both classification and regression trees and multilayer perceptron achieved an accuracy of 86.48%. Multielement profile combining with isotope ratio could be a more effective method. Rapisarda et al. (2005) determined the contents of Ca, K, Mg, P, N, $\delta^{15}\text{N}$ of amino acid and pulp proteins, combining with the values of total acid, total soluble solids, vitamin C, synephrine content, and developed a method to discriminate the organic and conventional orange juices. The results indicated that total N and synephrine contents were significantly higher in conventional fruits, whereas the $\delta^{15}\text{N}_{\text{‰}}$ values were higher in the organic ones, due to the different kinds of nitrogen fertilization of the soil in organically and conventionally managed farms. These new markers, linked to nitrogen metabolism, identified in this research by linear discriminant analysis of the data constituted a useful tool to differentiate organic citrus fruits or juices from conventional ones. However, $\delta^{15}\text{N}$ has seldom been used successfully as the sole criterion for organic and conventional fruit juice differentiation, because of the potential overlap between the $\delta^{15}\text{N}$ signatures of organic and conventionally produced plant products result from organic fertilizers by conventional farmers or the marketing of organic produce as conventional (Inácio, Chalk and Magalhães 2015; Inácio et al. 2020). Magdas, Dehelean, and Puscas (2012) determined H, C, O stable isotope ratios and the contents of heavy metals, Cu, Cr, Ni, Zn, Pb, Co, As, Cd and U, of 31 Romanian organic apple juices. The mean values of $\delta^{18}\text{O} = -4.2\text{‰}$, $\delta\text{D} = -46.5\text{‰}$, $\delta^{13}\text{C} = -28.2\text{‰}$, Ni, Zn, Cu, Cr vary between: 10–103 $\mu\text{g/L}$, 47–523 $\mu\text{g/L}$, 35.6–1224 $\mu\text{g/L}$, 10.6–252 $\mu\text{g/L}$, while Pb (0.02–11.02 $\mu\text{g/L}$), Co (0.3–3.76 $\mu\text{g/L}$), Cd (0.2–1.06 $\mu\text{g/L}$), As (0.18–1.14 $\mu\text{g/L}$), U (0.02–0.52 $\mu\text{g/L}$) were used to establish the database which could be used for adulteration and authenticity testing.

4.6. Fluorescence spectroscopy

FS, which can generate a signal containing information concerning all the fluorescent compounds within the sample, has been used for food sample authenticity determination (Lenhardt et al. 2015; Reid, O'Donnell, and Downey 2006), also for dilution and pulp wash addition of fruit juice (Petrus and Attaway 1980; Petrus, Fellers, and Anderson

1984). Recently, to characterize products from different berry fruit species (chokeberry, blackcurrant, raspberry and strawberry), the lowest error among the constructed PLS-DA models based on total FS and total synchronous FS of 4.42% was obtained for single synchronous FS measured at Delta lambda = 40 nm (Sikorska, Włodarska, and Khmelinskii 2020). Ammari, Redjda, and Rutledge (2015) used 3D-front-face FS followed by Independent Components Analysis to assess the adulteration of orange juice by grapefruit juice. The results clearly indicated that frauds can be detected at percentages as low as 1%.

The feasibility of FS for extraneous adulterants detection in fruit juices was evaluated. A fluorescent probe technique of double quantum dots was developed for sucrose sirup and artificial fruit powder detection in orange juice. Pure and adulterated orange juices were characterized by their different quenching patterns of the two separate and strong fluorescent peaks generated by the double quantum dots. A class model of pure orange juices was developed using one-class PLS after second-order derivatives transformation, and the model could detect at 5.0% (w/w) of sucrose sirup and 2.0% (w/w) of artificial fruit powder with a sensitivity of 97.8% and specificity of 77.0% (Xu et al. 2019). The usage of FS as a mean for discrimination between commercial NFC and FC apple juice was also studied. The discrimination results obtained from PLS-DA model based on unfolded total synchronous FS were cross-validation and external validation error rates of 0.05 and 0.06, respectively. The results also suggested the fluorescence of non-enzymatic browning products may significantly contribute to the differentiation of FC and NFC juices (Włodarska, Khmelinskii, and Sikorska 2018).

4.7. Electronic nose

EN uses an association of several sensitive elements on which volatile compounds get bound; this adsorption induces an alteration of the electrical signal of these elements. The outputs generated by these elementary detectors could be processed using chemometrics methods (Roussel et al. 2003). The application of an EN enables rapid analysis of the volatile compounds from food samples. Due to the fact that EN provides chemical profiling of natural products, it can be a powerful tool for authentication in combination with chemometrics (Róžańska, Dymerski, and Namieśnik 2018). It was usually used to analyze the volatile compound mixture as a whole, and it could also combine with GC to improve the resolving ability (Róžańska, Dymerski, and Namieśnik 2018; Wu, Yue, et al. 2018).

The researches of EN in discrimination of fruit juices from different species and varieties was carried out. For the classification of 100% NFC orange and apple juices, EN based on ultra-fast GC coupled with supervised statistical methods could allow to distinguish juice samples containing only 1.0% of adulteration with each other (Róžańska, Dymerski, and Namieśnik 2018). There are many species and varieties of biologically similar fruits, including some hybrid ones. Rapid discriminating evaluation of fruits'

botanical origin due to the allergen contents and quality control requirement (Lubinska-Szczygeł et al. 2018; Wu, Yue, et al. 2018). Three citrus fruits were analyzed using EN based on ultrafast GC. The results indicated it could be a novel analytical tool for hybrid fruits' classification due to their botanical origin (Lubinska-Szczygeł et al. 2018). EN was also used to characterize and classify apple juices according to variety. It was able to detect the juices prepared by 8 different varieties. With the help of LDA, the result showed a perfect discrimination of apple juices based on varieties (Wu et al. 2017). However, there is a research indicating EN is not well suited to white grape juice variety classification with calibration error rate of 41.3% and a leave-one-out cross-validation prediction error rate of 47.1% in constructed model (Roussel et al. 2003).

4.8. Others

Other untargeted techniques, such as multi-physicochemical variables, UV-VIS spectroscopy, capacitive sensor, have also been used for untargeted fruit juice authenticity determination.

To detect the adulteration with sugar, water etc. in orange juice, Das, Nandeshwar, and Phadke (2015) used a fractance type capacitive sensor, which gives different constant phase angle in the frequency range 2 kHz to 20 kHz when dipped in the different polarizing medium. The performance of the fractance type capacitive sensor indicates that it could be possible to identify or detect the adulteration of orange juice by observing the changes of the phase angle of the sensor. Euclidean distance of unknown sample can also be calculated with multiple numbers of known samples by LDA algorithm and the shortest distance sample gives its best characteristics. Usually, a physicochemical variable of fruit juice could be used for the targeted analysis, however, multi-physicochemical variables combining with chemometrics could also be an untargeted method for fruit juice authentication. A set of physicochemical variables obtained from orange juice, and the model constructed could detect adulterations starting from about 15% of dilution and later masking by the addition of sugar (Vaira et al. 1999).

Solid phase extraction-thin layer chromatography (SPE-TLC) was used for the adulterants detection by acquiring the fingerprints of lime juices. Combining with colorimetric analysis, the developed SPE-TLC method could be used to reveal the adulteration of commercial samples (Khodadadi et al. 2018). UV-VIS spectroscopy and chemometrics were used as a useful screening tool to assess addition of filler juices and water to pomegranate juices (Boggia et al. 2013).

5. Novel targeted markers by untargeted analysis

Untargeted analysis could detect unexpected deviations by chemometrics, even unknown novel markers. After identification and verification, they could be used for further targeted analysis. It represents a new emerging strategy in juice authenticity determination. The reported novel targeted

markers found by untargeted were summarized and shown in Table 2.

LC-MS based untargeted metabolomics is a powerful, highly effective approach to discover novel robust and unique markers for targeted analysis by comparing the metabolic profiles (Jandrić and Cannavan 2017). Based on the untargeted metabolomics analysis, OPLS-DA analysis was used to highlight the markers to differentiate Valencia and foreign classes. A novel useful season-independent marker, citrussin D was found. It could be used to rapidly differentiate the Valencia oranges against southern ones by targeted analysis (Diaz et al. 2014). Jandrić et al. (2014) optimized a targeted metabolomics after his research of untargeted metabolomics on mutual adulteration of orange and grapefruit juices. They characterized and identified 15 novel markers, which were used in the following validation process, and adulteration could be detected at 1%. Jandrić et al. (2017) also identified 13 novel markers, which were responsible for discriminating citrus fruit juices, and orange juices of various botanical/geographical origin based on the untargeted metabolomics. The ratios of novel markers identified in untargeted metabolomics profile are advantageous methods for fruit juice authenticity determination. To determine the citrus juice adulteration, 9 novel markers were identified in untargeted analysis. A quantitative method was then optimized for the analysis of these novel markers, and the ratios of limonin glucoside to hesperidin, narirutin, and didymin; narirutin to hesperidin and vicenin-2; didymin to hesperidin and narirutin; and vicenin-2 to didymin were then used to detect citrus juice adulteration (orange, mandarin, and grapefruit within each other) down to 2% (Jandrić et al. 2017). As for NFC and FC orange juices, they could also be differentiated by a LC-MS based method. 91 and 42 potential markers were determined in positive and negative ion modes by untargeted methods. And thirteen of them, L-glutamine, carvone, erucamide, lysoPE (16:0/0:0), oleic acid, α -linolenic acid and 7 tripeptides (reported for the first time in orange juice), were identified. Furthermore, a PLS-DA model, based on all the potential markers in positive mode by direct analysis in real time mass spectrometry-quadrupole time of flight (DART-QTOF) with 9 s acquisition time, was constructed and validated with 97% and 95% accuracy for training and test. The model was applied to commercial samples successfully (Xu, Xu, Kelly, et al. 2020).

GC-MS could illustrate the differences, identify novel markers of volatile compounds in juices, and provide useful access to differentiate juices (Wu et al. 2017). GC-MS profile analysis on different avocado varieties was carried out, and a total of 27 compounds were quantified (and 7 compounds were also quantified by GC-FID in this paper). Quinic and *p*-coumaric acids, epicatechin and quercetin as the novel markers for varieties discrimination were determined by PCA (Hurtado-Fernandez et al. 2014). For the classification of origin and cultivar of clarified apple juices, Gan, Soukoulis, and Fisk (2014) studied the volatile profile in conjunction with PLS-DA. The models generated were robust enough to reliably discriminate apple juices prepared from different varieties (100% correct classification by

Table 2. The novel markers found by untargeted analysis for targeted analysis.

Fruit juice types	Equipment	Chemometrics	Novel markers	Application	References
Orange	UHPLC-QTOF	OPLS-DA	Citrusin D	Discriminating the Valencia oranges against southern oranges	Diaz et al. 2014
Orange	UHPLC-QTOF	OPLS-DA	L-glutamine, carvone, erucamide, lysoPE (16:0/0:0), oleic acid, α -linolenic acid and 7 tripeptides	Discriminating the orange juices from concentrate or not	Xu, Xu, Kelly, et al. 2020
Orange and grapefruit	UPLC-QTOF	OPLS-DA	Hesperidine, neohesperidine, limonin-17- β -D-glucopyranoside, nomilinin-17-b- β -glucopyranoside, obacunonic acid-17- β -Dglucopyranoside, nomilinic acid-17- β -D-glucopyranoside, narirutin, naringin, isosakuranetin-7-O-rutinoside, daecetyl nomilinic acid-17- β -D-glucopyranoside, S-synapiylglutathione, N-L-glutamyl-S-synapyl-L-cysteine, L-(-)-Phenylalanine and 1-O- β -D-glucopyranoside sinapate	Detecting orange and grapefruit juices adulteration within each other	Jandrić et al. 2014
Orange mandarin, and grapefruit	UPLC-QTOF	OPLS-DA	Ratios of limonin glucoside to hesperidin, narirutin, and didymin; narirutin to hesperidin and vicenin-2; didymin to hesperidin and narirutin; and vicenin-2 to didymin	Detecting orange, mandarin, and grapefruit juices adulteration within each other	Jandrić et al. 2017
Avocado	GC-FID/APCI-TOF	PCA	Quinic and p-coumaric acids, epicatechin and quercetin	Discriminating the avocado varieties	Hurtado-Fernandez et al. 2014
Apple	GC-MS/APCI-MS	PLS-DA	hexanal, trans-2-hexenal, 1-hexanol, 1-butanol and cis-3-hexenol	Discriminating the cultivar and geographical origin	Gan, Soukoulis, and Fisk 2014
Orange	GC-MS/MS	PLS	D-carvone and β -terpineol	Discriminating HHP-treated and pasteurized orange juice	Bi et al., 2020
Orange	^1H NMR	PCA	dimethylproline	Detecting the pulp wash addition	Le Gall, Puaud, and Colquhoun 2001
Mango	^1H NMR	PCA	arginine, histidine, phenylalanine, glutamine, shikimic acid, and trigonelline	Discriminating the mango cultivars	Koda et al. 2012
Lemon	SPE-NMR	–	Sinensetin	Detecting orange, blood orange, mandarin, clementine, cravo and tangerine juices adulteration	Lehnert, Schmidt, and Ara 2017

external validation), and apple juices prepared from geographical provenance of apple (94.2% correct classification by external validation). Furthermore, they revealed that alkyl esters, carbonyl compounds (hexanal, trans-2-hexenal) and alcohols (1-hexanol, 1-butanol, cis-3-hexenol) as novel significant discriminating power both in terms of cultivar and geographical origin. As for different processing methods, after comparing the volatile profiles of high hydrostatic pressure and pasteurization orange juice, d-carvone and β -terpineol were determined as novel markers of HHP-treated and pasteurized orange juice, respectively (Bi et al. 2020).

Speaking of NMR, some novel markers for targeted analysis were also found. Sinensetin (higher than 0.015 mg/L) in lemon juice indicates the adulteration of other citrus (orange, blood orange, mandarin, clementine, cravo or tangerine) juices (Lehnert, Schmidt, and Ara 2017), arginine, histidine, phenylalanine, glutamine, shikimic acid, and trigonelline for cultivar discrimination of mango (Koda et al.

2012), and dimethylproline for pulp wash addition in orange juice (Le Gall, Puaud, and Colquhoun 2001).

Although less effective than untargeted analysis, the targeted method with novel markers is simpler, requires less sophisticated instrumentation, and the data is more easily analyzed and interpreted, making it potentially more applicable for routine analysis (Jandrić et al. 2017). The problem may be the consistency and stability of the novel markers.

6. Conclusions and perspectives

In conclusion, diverse research work has been done to determine the authenticity of fruit juices, and achieved good results. For targeted analysis, tremendous efforts have been made to determine the numerous specific ingredient contents of fruit juices, including stable isotopes, phenolics, carbohydrates, organic acids, volatile components, DNAs, amino acids and proteins, as well as carotenoids. As for untargeted methods, metabolomics methods (based on LC-

MS, GC-MS and NMR), IR, fluorescence spectroscopy and metal profiles with plenty multivariate statistical methods have been applied for the authenticity determination. Targeted analysis is usually more sensitive than untargeted analysis, because the method is optimized for the specific ingredient analysis. However, if the fraud faced is not elaborate or the specific ingredient is unclear, untargeted analysis would be the more efficient solution. It collects multiple data points from the sample without pre-defined list, which means it may not be known which ingredients are being measured or what they indicate. Therefore, new specific ingredients could be found. But it requires extensive data processing, multivariate statistical analysis and modeling. All these work means a lot to the protection of consumer rights and interests. These developments of fraud determination technologies promote the healthy development of fruit juice industry.

While, the juice market is still booming. NFC fruit juice has got more and more attention, and, some functional fruit juices are thriving. Thereupon, new sophisticated counterfeiting means during processing and transporting are also emerging, such as the adulteration of NFC juice with FC juice, non-thermally processed juice with thermally processed juice, and functional juice frauds. The difference between these juices may be even more minor. Most importantly, there are limited methods or targeted markers to count on. Only the authenticating technique keeps abreast of the counterfeiting means, fruit juice industry could be flourishing.

Therefore, developing new authenticating techniques is imperative. Discovering novel potential markers for targeted methods based on untargeted approaches has been applied to trace food adulteration successfully. However, with restriction to the separating ability, coverage, detection limit and dynamic range of the instruments used in untargeted methods, some markers might be neglected. Some advances in analytical chemistry could be used to solve these problems. Pseudotargeted metabolomics approach has been applied to discover markers of disease as well as fruit juices (Xu, Xu, Wang, et al. 2020). Combination of qualitative ability of high-resolution mass spectrometry and quantitative ability of triple quadrupole mass spectrometry, pseudotargeted approach has advantages in coverage, reproducibility, sensitivity, and dynamic range (Zha et al. 2018). Also, with the introduction of ion mobility mass spectrometry (IM-MS), the next dimension for qualitative analysis, i.e. the drift time, data set acquired using LC-IM-MS may contain additional information, thus creating a further fifth data dimension for marker qualitative analysis (Cajka and Fiehn 2016). And to increase the efficiency of authentication, some rapid detection method, such as DART-QTOF, rapid evaporative ionization mass spectrometry, soft ionization by chemical reaction in transfer, can be introduced. The analysis time could be limited to seconds with high accuracy as well (Xu, Xu, Kelly, et al. 2020).

However, determining if a fruit juice is exactly as declared is not easy. Each analytical approach has its limitations which restricts its applicability. We should integrate

and establish an international comprehensive specification for fruit juices, based on the profiles generated from analyses combined the information from existing databases (such as the AIJN developed by European Juice Association) and published literatures, which can be utilized to authenticate fruit juice efficiently. Therefore, it is hopeful that with the development of novel analytical approaches, construction of comprehensive specifications as well as the corresponding punitive measures, the necessary expense for fruit juice fraud will be increased at a level which makes fraud extremely risky and increasingly uneconomical. Thus, a healthy fruit juice market could be established and maintained.

Declaration of interest statement

The authors declare no conflict of interest.

Funding

This work was supported by the National Key R&D Program of China under Grant 2017YFD0400705.

ORCID

Zhenzhen Xu  <http://orcid.org/0000-0003-4111-3530>

References

- Abad-García, B., L. A. Berrueta, S. Garmón-Lobato, A. Urkaregi, B. Gallo, and F. Vicente. 2012. Chemometric characterization of fruit juices from Spanish cultivars according to their phenolic compound contents: I. Citrus fruits. *Journal of Agricultural and Food Chemistry* 60 (14):3635–44. doi: [10.1021/jf300022u](https://doi.org/10.1021/jf300022u).
- Abad-García, B., S. Garmón-Lobato, M. B. Sánchez-Ilárduya, L. A. Berrueta, B. Gallo, F. Vicente, and R. M. Alonso-Salces. 2014. Polyphenolic contents in Citrus fruit juices: Authenticity assessment. *European Food Research and Technology* 238 (5):803–18. doi: [10.1007/s00217-014-2160-9](https://doi.org/10.1007/s00217-014-2160-9).
- Aldeguer, M., M. López-Andreo, J. A. Gabaldón, and A. Puyet. 2014. Detection of mandarin in orange juice by single-nucleotide polymorphism qPCR assay. *Food Chemistry* 145:1086–91. doi: [10.1016/j.foodchem.2013.09.002](https://doi.org/10.1016/j.foodchem.2013.09.002).
- Allegrone, G., F. Belliardo, and P. Cabella. 2006. Comparison of volatile concentrations in hand-squeezed juices of four different lemon varieties. *Journal of Agricultural and Food Chemistry* 54 (5):1844–8. doi: [10.1021/jf051206s](https://doi.org/10.1021/jf051206s).
- Ammari, F., L. Redjda, and D. N. Rutledge. 2015. Detection of orange juice frauds using front-face fluorescence spectroscopy and independent components analysis. *Food Chemistry* 168:211–7. doi: [10.1016/j.foodchem.2014.06.110](https://doi.org/10.1016/j.foodchem.2014.06.110).
- Antolovich, M., X. Li, and K. Robards. 2001. Detection of adulteration in Australian orange juices by stable carbon isotope ratio analysis (SCIRA). *Journal of Agricultural and Food Chemistry* 49 (5):2623–6. doi: [10.1021/jf001384f](https://doi.org/10.1021/jf001384f).
- Arana, V. A., J. Medina, R. Alarcon, E. Moreno, L. Heintz, H. Schafer, and J. Wist. 2015. Coffee's country of origin determined by NMR: The Colombian case. *Food Chemistry* 175:500–6. doi: [10.1016/j.foodchem.2014.11.160](https://doi.org/10.1016/j.foodchem.2014.11.160).
- Asadpoor, M., M. Ansarin, and M. Nemati. 2014. Amino acid profile as a feasible tool for determination of the authenticity of fruit juices. *Advanced Pharmaceutical Bulletin* 4 (4):359–62. doi: [10.5681/apb.2014.052](https://doi.org/10.5681/apb.2014.052).

- Ballester-Tomas, L., J. A. Prieto, J. V. Gil, M. Baeza, and F. Randez-Gil. 2017. The Antarctic yeast *Candida sake*: Understanding cold metabolism impact on wine. *International Journal of Food Microbiology* 245:59–65. doi: [10.1016/j.ijfoodmicro.2017.01.009](https://doi.org/10.1016/j.ijfoodmicro.2017.01.009).
- Benabdelkamel, H., L. D. Donna, F. Mazzotti, A. Naccarato, G. Sindona, A. Tagarelli, and D. Taverna. 2012. Authenticity of PGI “clementine of Calabria” by multielement fingerprint. *Journal of Agricultural and Food Chemistry* 60 (14):3717–26. doi: [10.1021/jf2050075](https://doi.org/10.1021/jf2050075).
- Berrueta, L. A., R. M. Alonso-Salces, and K. Héberger. 2007. Supervised pattern recognition in food analysis. *Journal of Chromatography. A* 1158 (1-2):196–214. doi: [10.1016/j.chroma.2007.05.024](https://doi.org/10.1016/j.chroma.2007.05.024).
- Bi, S., S. Sun, F. Lao, X. Liao, and J. Wu. 2020. Gas chromatography-mass spectrometry combined with multivariate data analysis as a tool for differentiating between processed orange juice samples on the basis of their volatile markers. *Food Chemistry* 311:125913. doi: [10.1016/j.foodchem.2019.125913](https://doi.org/10.1016/j.foodchem.2019.125913).
- Bocharova, O., S. Reshta, M. Bocharova, and V. Eshtokin. 2017. Evaluation of orange juice authenticity in respect of added food flavors using dilution index. *Journal of Food Processing and Preservation* 41 (6):e13221. doi: [10.1111/jfpp.13221](https://doi.org/10.1111/jfpp.13221).
- Bocharova, O. V., S. P. Reshta, M. Y. Bocharova, and V. I. Eshtokin. 2018. Determination of apple juice authenticity using gas chromatography-mass spectrometry, volt-ampere and new conductometric methods. *Journal of the Science of Food and Agriculture* 98 (12):4692–9. doi: [10.1002/jsfa.9003](https://doi.org/10.1002/jsfa.9003).
- Boggia, R., M. C. Casolino, V. Hysenaj, P. Oliveri, and P. Zunin. 2013. A screening method based on UV-Visible spectroscopy and multivariate analysis to assess addition of filler juices and water to pomegranate juices. *Food Chemistry* 140 (4):735–41. doi: [10.1016/j.foodchem.2012.11.020](https://doi.org/10.1016/j.foodchem.2012.11.020).
- Bong, Y.-S., K.-S. Lee, W.-J. Shin, and J.-S. Ryu. 2008. Comparison of the oxygen and hydrogen isotopes in the juices of fast-growing vegetables and slow-growing fruits. *Rapid Communications in Mass Spectrometry* 22 (18):2809–12. doi: [10.1002/rcm.3663](https://doi.org/10.1002/rcm.3663).
- Borges, E. M., D. A. Volmer, E. Brandelero, J. M. L. N. Gelinski, M. Gallimberti, and F. Barbosa. 2016. Monitoring the authenticity of organic grape juice via chemometric analysis of elemental data. *Food Analytical Methods* 9 (2):362–9. doi: [10.1007/s12161-015-0191-x](https://doi.org/10.1007/s12161-015-0191-x).
- Borges, G., and A. Crozier. 2012. HPLC-PDA-MS fingerprinting to assess the authenticity of pomegranate beverages. *Food Chemistry* 135 (3):1863–7. doi: [10.1016/j.foodchem.2012.05.108](https://doi.org/10.1016/j.foodchem.2012.05.108).
- Bosmali, I., I. Ganopoulos, P. Madesis, and A. Tsiftaris. 2012. Microsatellite and DNA-barcode regions typing combined with high resolution melting (HRM) analysis for food forensic uses: A case study on lentils (*Lens culinaris*). *Food Research International* 46 (1):141–7. doi: [10.1016/j.foodres.2011.12.013](https://doi.org/10.1016/j.foodres.2011.12.013).
- Botoran, O. R., R. E. Ionete, M. G. Miricioiu, D. Costinel, G. L. Radu, and R. Popescu. 2019. Amino acid profile of fruits as potential fingerprints of varietal origin. *Molecules* 24 (24):4500. doi: [10.3390/molecules24244500](https://doi.org/10.3390/molecules24244500).
- Boudet, A. M. 2007. Evolution and current status of research in phenolic compounds. *Phytochemistry* 68 (22-24):2722–35. doi: [10.1016/j.phytochem.2007.06.012](https://doi.org/10.1016/j.phytochem.2007.06.012).
- Cagliero, C., C. Bicchì, C. Cordero, P. Rubiolo, B. Sgorbini, and E. Liberto. 2012. Fast headspace-enantioselective GC-mass spectrometric-multivariate statistical method for routine authentication of flavoured fruit foods. *Food Chemistry* 132 (2):1071–9. doi: [10.1016/j.foodchem.2011.10.106](https://doi.org/10.1016/j.foodchem.2011.10.106).
- Caja, M. M., G. P. Blanch, M. Herraiz, and M. L. Ruiz Del Castillo. 2004. On-line reversed-phase liquid chromatography-gas chromatography coupled to mass spectrometry for enantiomeric analysis of chiral compounds in fruit beverages. *Journal of Chromatography. A* 1054 (1-2):81–5. doi: [10.1016/j.chroma.2004.04.050](https://doi.org/10.1016/j.chroma.2004.04.050).
- Cajka, T., and O. Fiehn. 2016. Toward merging untargeted and targeted methods in mass spectrometry-based metabolomics and lipidomics. *Analytical Chemistry* 88 (1):524–45. doi: [10.1021/acs.analchem.5b04491](https://doi.org/10.1021/acs.analchem.5b04491).
- Camin, F., M. Perini, L. Bontempo, and L. Giongo. 2009. Multi-element (H, C, N, O) stable isotope characterization of blueberries. *Acta Horticulturae* 810:697–703.
- Cicero, N., C. Corsaro, A. Salvo, S. Vasi, S. V. Giofrè, V. Ferrantelli, V. Di Stefano, D. Mallamace, and G. Dugo. 2015. The metabolic profile of lemon juice by proton HR-MAS NMR: The case of the PGI Interdonato lemon of Messina. *Natural Product Research* 29 (20):1894–902. doi: [10.1080/14786419.2015.1012166](https://doi.org/10.1080/14786419.2015.1012166).
- Codex Alimentarius Commission. 2005. CODEX STAN 247-2005: Codex general standard for fruit juices and nectars. Accessed June 17, 2020. www.fao.org/input/download/standards/10154/CXS_247e.pdf.
- Cuny, M., G. L. Gall, I. J. Colquhoun, M. Lees, and D. N. Rutledge. 2007. Evolving window zone selection method followed by independent component analysis as useful chemometric tools to discriminate between grapefruit juice, orange juice and blends. *Analytica Chimica Acta* 597 (2):203–13. doi: [10.1016/j.aca.2007.07.018](https://doi.org/10.1016/j.aca.2007.07.018).
- Cuny, M., E. Vigneau, G. L. Gall, I. Colquhoun, M. Lees, and D. N. Rutledge. 2008. Fruit juice authentication by ¹H NMR spectroscopy in combination with different chemometrics tools. *Analytical and Bioanalytical Chemistry* 390 (1):419–27. doi: [10.1007/s00216-007-1708-y](https://doi.org/10.1007/s00216-007-1708-y).
- Das, S., V. J. Nandeshwar, and G. S. Phadke. 2015. 2015 IEEE International WIE Conference on Electrical and Computer Engineering, WIECON-ECE 2015. Dhaka, Bangladesh.
- Dasenaki, M. E., S. K. Drakopoulou, R. Aalizadeh, and N. S. Thomaidis. 2019. Targeted and untargeted metabolomics as an enhanced tool for the detection of pomegranate juice adulteration. *Foods* 8 (6):212. doi: [10.3390/foods8060212](https://doi.org/10.3390/foods8060212).
- de Pascual-Teresa, S., and M. T. Sanchez-Ballesta. 2008. Anthocyanins: From plant to health. *Phytochemistry Reviews* 7 (2):281–99. doi: [10.1007/s11101-007-9074-0](https://doi.org/10.1007/s11101-007-9074-0).
- Delpino-Rius, A., J. Eras, F. Gatiús, M. Balcells, and R. Canela-Garayoa. 2019. Combined analysis of primary metabolites and phenolic compounds to authenticate commercial monovarietal peach purees and pear juices. *Molecules* 24 (18):3289. doi: [10.3390/molecules24183289](https://doi.org/10.3390/molecules24183289).
- Di Anibal, C. V., I. Ruisánchez, and M. P. Callao. 2011. High-resolution ¹H nuclear magnetic resonance spectrometry combined with chemometric treatment to identify adulteration of culinary spices with Sudan dyes. *Food Chemistry* 124 (3):1139–45. doi: [10.1016/j.foodchem.2010.07.025](https://doi.org/10.1016/j.foodchem.2010.07.025).
- Díaz, R., O. J. Pozo, J. V. Sancho, and F. Hernandez. 2014. Metabolomic approaches for orange origin discrimination by ultra-high performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry. *Food Chemistry* 157:84–93. doi: [10.1016/j.foodchem.2014.02.009](https://doi.org/10.1016/j.foodchem.2014.02.009).
- Díaz-García, M. C., J. M. Obón, M. R. Castellar, J. Collado, and M. Alacid. 2013. Quantification by UHPLC of total individual polyphenols in fruit juices. *Food Chemistry* 138 (2-3):938–49. doi: [10.1016/j.foodchem.2012.11.061](https://doi.org/10.1016/j.foodchem.2012.11.061).
- Difonzo, G., K. Vollmer, F. Caponio, A. Pasqualone, R. Carle, and C. B. Steingass. 2019. Characterisation and classification of pineapple (*Ananas comosus* [L.] Merr.) juice from pulp and peel. *Food Control* 96:260–70. doi: [10.1016/j.foodcont.2018.09.015](https://doi.org/10.1016/j.foodcont.2018.09.015).
- Ding, J., J. Jia, L. Yang, H. Wen, C. Zhang, W. Liu, and D. Zhang. 2004. Validation of a rice specific gene, sucrose phosphate synthase, used as the endogenous reference gene for qualitative and real-time quantitative PCR detection of transgenes. *Journal of Agricultural and Food Chemistry* 52 (11):3372–7. doi: [10.1021/jf049915d](https://doi.org/10.1021/jf049915d).
- Dona, A. C., M. Kyriakides, F. Scott, E. A. Shephard, D. Varshavi, K. Veselkov, and J. R. Everett. 2016. A guide to the identification of metabolites in NMR-based metabolomics/metabonomics experiments. *Computational and Structural Biotechnology Journal* 14:135–53. doi: [10.1016/j.csbj.2016.02.005](https://doi.org/10.1016/j.csbj.2016.02.005).
- Dong, H., Z. Ning, L. Yu, L. Li, L. Lin, and J. Huang. 2007. Preparative separation and identification of the flavonoid phlorhizin from the crude extract of *Lithocarpus polystachyus* Rehd. *Molecules* 12 (3):552–62. doi: [10.3390/12030552](https://doi.org/10.3390/12030552).

- Drivelos, S. A., and C. A. Georgiou. 2012. Multi-element and multi-isotope-ratio analysis to determine the geographical origin of foods in the European Union. *TrAC Trends in Analytical Chemistry* 40: 38–51. doi: [10.1016/j.trac.2012.08.003](https://doi.org/10.1016/j.trac.2012.08.003).
- Dugo, P., D. Giuffrida, M. Herrero, P. Donato, and L. Mondello. 2009. Epoxycarotenoids esters analysis in intact orange juices using two-dimensional comprehensive liquid chromatography. *Journal of Separation Science* 32 (7):973–80. doi: [10.1002/jssc.200800696](https://doi.org/10.1002/jssc.200800696).
- Dunn, W. B., and D. I. Ellis. 2005. Metabolomics: Current analytical platforms and methodologies. *TrAC Trends in Analytical Chemistry* 24:285–94.
- Ehling, S., and S. Cole. 2011. Analysis of organic acids in fruit juices by liquid chromatography-mass spectrometry: An enhanced tool for authenticity testing. *Journal of Agricultural and Food Chemistry* 59 (6):2229–34. doi: [10.1021/jf104527e](https://doi.org/10.1021/jf104527e).
- Ellis, D. I., J. Ellis, H. Muhamadali, Y. Xu, A. B. Horn, and R. Goodacre. 2016. Rapid, high-throughput, and quantitative determination of orange juice adulteration by Fourier-transform infrared spectroscopy. *Analytical Methods* 8 (28):5581–6. doi: [10.1039/C6AY01480A](https://doi.org/10.1039/C6AY01480A).
- Everstine, K., J. Spink, and S. Kennedy. 2013. Economically motivated adulteration (EMA) of food: Common characteristics of EMA incidents. *Journal of Food Protection* 76 (4):723–35. doi: [10.4315/0362-028X.JFP-12-399](https://doi.org/10.4315/0362-028X.JFP-12-399).
- Fabiani, A., A. Versari, G. P. Parpinello, M. Castellari, and S. Galassi. 2002. High-performance liquid chromatographic analysis of free amino acids in fruit juices using derivatization with 9-fluorenylmethyl-chloroformate. *Journal of Chromatographic Science* 40 (1): 14–8. doi: [10.1093/chromsci/40.1.14](https://doi.org/10.1093/chromsci/40.1.14).
- Faria, A., and C. Calhau. 2011. The bioactivity of pomegranate: Impact on health and disease. *Critical Reviews in Food Science and Nutrition* 51 (7):626–34. doi: [10.1080/10408391003748100](https://doi.org/10.1080/10408391003748100).
- Faria, M. A., A. Magalhães, M. E. Nunes, and M. B. P. P. Oliveira. 2013. High resolution melting of trnL amplicons in fruit juices authentication. *Food Control* 33 (1):136–41. doi: [10.1016/j.foodcont.2013.02.020](https://doi.org/10.1016/j.foodcont.2013.02.020).
- Fernandez de Simon, B., J. Perez-Illarbe, T. Hernandez, C. Gomez-Cordoves, and I. Estrella. 1992. Importance of phenolic compounds for the characterization of fruit juices. *Journal of Agricultural and Food Chemistry* 40 (9):1531–5. doi: [10.1021/jf00021a012](https://doi.org/10.1021/jf00021a012).
- Fischer, U. A., A. V. Jaksch, R. Carle, and D. R. Kammerer. 2013. Influence of origin source, different fruit tissue and juice extraction methods on anthocyanin, phenolic acid, hydrolysable tannin and isolaricresinol contents of pomegranate (*Punica granatum* L.) fruits and juices. *European Food Research and Technology* 237 (2):209–21. doi: [10.1007/s00217-013-1981-2](https://doi.org/10.1007/s00217-013-1981-2).
- Fischerzorn, M., and V. Ara. 2007. Pomegranate juice—Chemical composition and potential adulteration. *Fruit Processing* 17:204–13.
- Fromm, M., S. Bayha, R. Carle, and D. R. Kammerer. 2012. Characterization and quantitation of low and high molecular weight phenolic compounds in apple seeds. *Journal of Agricultural and Food Chemistry* 60 (5):1232–42. doi: [10.1021/jf204623d](https://doi.org/10.1021/jf204623d).
- Gan, H. H., C. Soukoulis, and I. Fisk. 2014. Atmospheric pressure chemical ionisation mass spectrometry analysis linked with chemometrics for food classification—A case study: Geographical provenance and cultivar classification of monovarietal clarified apple juices. *Food Chemistry* 146:149–56. doi: [10.1016/j.foodchem.2013.09.024](https://doi.org/10.1016/j.foodchem.2013.09.024).
- Ganopoulos, I., A. Argiriou, and A. Tsaftaris. 2011. Microsatellite high resolution melting (SSR-HRM) analysis for authenticity testing of protected designation of origin (PDO) sweet cherry products. *Food Control* 22 (3–4):532–41. doi: [10.1016/j.foodcont.2010.09.040](https://doi.org/10.1016/j.foodcont.2010.09.040).
- Gil, M. I., F. A. Tomás-Barberán, B. Hess-Pierce, D. M. Holcroft, and A. A. Kader. 2000. Antioxidant activity of pomegranate juice and its relationship with phenolic composition and processing. *Journal of Agricultural and Food Chemistry* 48 (10):4581–9. doi: [10.1021/jf000404a](https://doi.org/10.1021/jf000404a).
- Giuffrida, D., P. Dugo, A. Salvo, M. Saitta, and G. Dugo. 2010. Free carotenoid and carotenoid ester composition in native orange juices of different varieties. *Fruits* 65 (5):277–84. doi: [10.1051/fruits/2010023](https://doi.org/10.1051/fruits/2010023).
- Gökmen, V., N. Artik, J. Acar, N. Kahraman, and E. Poyrazoğlu. 2001. Effects of various clarification treatments on patulin, phenolic compound and organic acid compositions of apple juice. *European Food Research and Technology* 213:194–9.
- Gómez-Ariza, J. L., M. J. Villegas-Portero, and V. Bernal-Daza. 2005. Characterization and analysis of amino acids in orange juice by HPLC-MS/MS for authenticity assessment. *Analytica Chimica Acta* 540 (1):221–30. doi: [10.1016/j.aca.2004.08.048](https://doi.org/10.1016/j.aca.2004.08.048).
- Gonzalez, J., E. Jamin, G. Remaud, Y. L. Martin, G. G. Martin, and M. L. Martin. 1998. Authentication of lemon juices and concentrates by a combined multi-isotope approach using SNIF-NMR and IRMS. *Journal of Agricultural and Food Chemistry* 46 (6):2200–5. doi: [10.1021/jf971066p](https://doi.org/10.1021/jf971066p).
- González, J., G. Remaud, E. Jamin, N. Naulet, and G. G. Martin. 1999. Specific natural isotope profile studied by isotope ratio mass spectrometry (SNIP – IRMS): $^{13}\text{C}/^{12}\text{C}$ ratios of fructose, glucose, and sucrose for improved detection of sugar addition to pineapple juices and concentrates. *Journal of Agricultural and Food Chemistry* 47 (6): 2316–21. doi: [10.1021/jf981093v](https://doi.org/10.1021/jf981093v).
- Gosch, C., H. Halbwirth, and K. Stich. 2010. Phloridzin: Biosynthesis, distribution and physiological relevance in plants. *Phytochemistry* 71 (8–9):838–43. doi: [10.1016/j.phytochem.2010.03.003](https://doi.org/10.1016/j.phytochem.2010.03.003).
- Guyon, F., P. Auberger, L. Gaillard, C. Loubanches, M. Viateau, N. Sabathié, M. H. Salagoity, and B. Médina. 2014. $^{13}\text{C}/^{12}\text{C}$ isotope ratios of organic acids, glucose and fructose determined by HPLC-co-IRMS for lemon juices authenticity. *Food Chemistry* 146:36–40. doi: [10.1016/j.foodchem.2013.09.020](https://doi.org/10.1016/j.foodchem.2013.09.020).
- Han, J., Y. Wu, W. Huang, B. Wang, C. Sun, Y. Ge, and Y. Chen. 2012. PCR and DHPLC methods used to detect juice ingredient from 7 fruits. *Food Control* 25 (2):696–703. doi: [10.1016/j.foodcont.2011.12.001](https://doi.org/10.1016/j.foodcont.2011.12.001).
- Hansen, A. M. S., H. L. Frandsen, and A. Fromberg. 2016. Authenticity of raspberry flavor in food products using SPME-chiral-GC-MS. *Food Science & Nutrition* 4 (3):348–54. doi: [10.1002/fsn3.296](https://doi.org/10.1002/fsn3.296).
- Hayasaka, Y., K. S. Adams, K. F. Pocock, G. A. Baldock, E. J. Waters, and P. B. Høj. 2001. Use of electrospray mass spectrometry for mass determination of grape (*Vitis vinifera*) juice pathogenesis-related proteins: A potential tool for varietal differentiation. *Journal of Agricultural and Food Chemistry* 49 (4):1830–9. doi: [10.1021/jf001163+](https://doi.org/10.1021/jf001163+).
- He, J., L. E. Rodriguez-Saona, and M. M. Giusti. 2007. Midinfrared spectroscopy for juice authentication-rapid differentiation of commercial juices. *Journal of Agricultural and Food Chemistry* 55 (11): 4443–52. doi: [10.1021/jf062715c](https://doi.org/10.1021/jf062715c).
- Hilt, P., A. Schieber, C. Yildirim, G. Arnold, I. Klaiber, J. Conrad, U. Beifuss, and R. Carle. 2003. Detection of phloridzin in strawberries (*Fragaria x ananassa* Duch.) by HPLC-PDA-MS/MS and NMR spectroscopy. *Journal of Agricultural and Food Chemistry* 51 (10): 2896–9. doi: [10.1021/jf021115k](https://doi.org/10.1021/jf021115k).
- Hofsommer, H., and S. Koswig. 1999. New analytical techniques for judging the authenticity of fruit juices. *Fruit Process* 12:471–9.
- Horn, P., P. Schaaf, B. Holbach, S. Hölzl, and H. Eschnauer. 1993. $^{87}\text{Sr}/^{86}\text{Sr}$ from rock and soil into vine and wine. *Zeitschrift für Lebensmittel-Untersuchung und -Forschung* 196 (5):407–9. doi: [10.1007/BF01190802](https://doi.org/10.1007/BF01190802).
- Houerou, G., S. D. Kelly, and M. J. Dennis. 1999. Determination of the oxygen-18/oxygen-16 isotope ratios of sugar, citric acid and water from single strength orange juice. *Rapid Communications in Mass Spectrometry* 13 (13):1257–62. doi: [10.1002/\(SICI\)1097-0231\(19990715\)13:13<1257::AID-RCM561>3.0.CO;2-G](https://doi.org/10.1002/(SICI)1097-0231(19990715)13:13<1257::AID-RCM561>3.0.CO;2-G).
- Hurtado-Fernandez, E., T. Pacchiarotta, E. Longueira-Suarez, O. A. Mayboroda, A. Fernandez-Gutierrez, and A. Carrasco-Pancorbo. 2013. Evaluation of gas chromatography-atmospheric pressure chemical ionization-mass spectrometry as an alternative to gas chromatography-electron ionization-mass spectrometry: Avocado fruit as example. *Journal of Chromatography. A* 1313:228–44. doi: [10.1016/j.chroma.2013.08.084](https://doi.org/10.1016/j.chroma.2013.08.084).
- Hurtado-Fernandez, E., T. Pacchiarotta, O. A. Mayboroda, A. Fernandez-Gutierrez, and A. Carrasco-Pancorbo. 2014. Quantitative characterization of important metabolites of avocado fruit by gas

- chromatography coupled to different detectors (APCI-TOF MS and FID). *Food Research International* 62:801–11. doi: [10.1016/j.foodres.2014.04.038](https://doi.org/10.1016/j.foodres.2014.04.038).
- Ídková, J., and J. Chmelík. 2001. Determination of saccharides in fruit juices by capillary electrophoresis and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. *Journal of Mass Spectrometry* 36 (4):417–21. doi: [10.1002/jms.144](https://doi.org/10.1002/jms.144).
- Inácio, C. d. T., J. C. Nunes, J. L. Andriolo, P. M. Chalk, S. J. Giacomini, L. De Conti, A. V. Krug, B. V. de Paula, and G. Brunetto. 2020. Organic, conventional and hydroponic vegetables: Can ^{15}N natural abundance of farm N inputs differentiate mode of production? *Scientia Horticulturae* 265 (109219):109219. doi: [10.1016/j.scienta.2020.109219](https://doi.org/10.1016/j.scienta.2020.109219).
- Inácio, C. T., P. M. Chalk, and A. M. Magalhães. 2015. Principles and limitations of stable isotopes in differentiating organic and conventional foodstuffs: 1. Plant products. *Critical Reviews in Food Science and Nutrition* 55 (9):1206–18. doi: [10.1080/10408398.2012.689380](https://doi.org/10.1080/10408398.2012.689380).
- Jamin, E., J. Gonzalez, I. Bengoechea, G. Kerneur, G. Remaud, C. Iriondo, and G. G. Martin. 1998. Proteins as intermolecular isotope reference for detection of adulteration of fruit juices. *Journal of Agricultural and Food Chemistry* 46 (12):5118–23. doi: [10.1021/jf980664g](https://doi.org/10.1021/jf980664g).
- Jamin, E., J. Gonzalez, G. Remaud, N. Naulet, and G. G. Martin. 1997. Detection of exogenous sugars or organic acids addition in pineapple juices and concentrates by C-13 IRMS analysis. *Journal of Agricultural and Food Chemistry* 45 (10):3961–7. doi: [10.1021/jf9701087](https://doi.org/10.1021/jf9701087).
- Jamin, E., J. Gonzalez, G. Remaud, N. Naulet, G. G. Martin, D. Weber, A. Rossmann, and H. L. Schmidt. 1997. Improved detection of sugar addition to apple juices and concentrates using internal standard C-13 IRMS. *Analytica Chimica Acta* 347 (3):359–68. doi: [10.1016/S0003-2670\(97\)00189-X](https://doi.org/10.1016/S0003-2670(97)00189-X).
- Jamin, E., R. Guérin, M. Rétif, M. Lees, and G. J. Martin. 2003. Improved detection of added water in orange juice by simultaneous determination of the oxygen-18/oxygen-16 isotope ratios of water and ethanol derived from sugars-site-specific natural isotope fractionation-NMR. *Journal of Agricultural and Food Chemistry* 51 (18):5202–6. doi: [10.1021/jf030167m](https://doi.org/10.1021/jf030167m).
- Jandrić, Z., and A. Cannavan. 2017. An investigative study on differentiation of citrus fruit/fruit juices by UPLC-QToF MS and chemometrics. *Food Control* 72:173–80. doi: [10.1016/j.foodcont.2015.12.031](https://doi.org/10.1016/j.foodcont.2015.12.031).
- Jandrić, Z., M. Islam, D. K. Singh, and A. Cannavan. 2017. Authentication of Indian citrus fruit/fruit juices by untargeted and targeted metabolomics. *Food Control* 72:181–8. doi: [10.1016/j.foodcont.2015.10.044](https://doi.org/10.1016/j.foodcont.2015.10.044).
- Jandrić, Z., D. Roberts, M. N. Rathor, A. Abraham, M. Islam, and A. Cannavan. 2014. Assessment of fruit juice authenticity using UPLC-QToF MS: A metabolomics approach. *Food Chemistry* 148:7–17. doi: [10.1016/j.foodchem.2013.10.014](https://doi.org/10.1016/j.foodchem.2013.10.014).
- Ježek, J., and M. Suhaj. 2001. Application of capillary isotachopheresis for fruit juice authentication. *Journal of Chromatography. A* 916 (1–2):185–9. doi: [10.1016/S0021-9673\(00\)01078-5](https://doi.org/10.1016/S0021-9673(00)01078-5).
- Jha, S. N., and S. Gunasekaran. 2010. Authentication of sweetness of mango juice using Fourier transform infrared-attenuated total reflection spectroscopy. *Journal of Food Engineering* 101 (3):337–42. doi: [10.1016/j.jfoodeng.2010.07.019](https://doi.org/10.1016/j.jfoodeng.2010.07.019).
- Karadeniz, F. 2004. Main organic acid distribution of authentic citrus juices in Turkey. *Turkish Journal of Agriculture and Forestry* 28:267–71.
- Kelly, J. F. D., and G. Downey. 2005. Detection of sugar adulterants in apple juice using Fourier transform infrared spectroscopy and chemometrics. *Journal of Agricultural and Food Chemistry* 53 (9):3281–6. doi: [10.1021/jf048000w](https://doi.org/10.1021/jf048000w).
- Kelly, S. D., C. Rhodes, J. H. Lofthouse, D. Anderson, C. E. Burwood, M. J. Dennis, and P. Brereton. 2003. Detection of sugar syrups in apple juice by $\delta(2)\text{H}$ per thousand and $\delta(13)\text{C}$ per thousand analysis of hexamethylenetetramine prepared from fructose. *Journal of Agricultural and Food Chemistry* 51 (7):1801–6. doi: [10.1021/jf021044p](https://doi.org/10.1021/jf021044p).
- Khodadadi, A., M. Nemati, E. Tamizi, and H. Nazemiyeh. 2018. Facile and accelerated method for detection of adulteration in commercially available lime juice products in Iranian market. *Pharmaceutical Sciences* 24 (2):148–56. doi: [10.1517/PS.2018.22](https://doi.org/10.1517/PS.2018.22).
- Koda, M., K. Furihata, F. Wei, T. Miyakawa, and M. Tanokura. 2012. Metabolic discrimination of mango juice from various cultivars by band-selective NMR spectroscopy. *Journal of Agricultural and Food Chemistry* 60 (5):1158–66. doi: [10.1021/jf2041438](https://doi.org/10.1021/jf2041438).
- Kolesnov, A., R. Filippova, I. Filatova, D. Zadorozhnyaya, and O. Maloshitskaya. 2014. Study of biologically fractionated stable oxygen isotopes ^{18}O and ^{16}O in pomegranate fruits from the caspian region. *Acta Horticulturae* 1017 (1017):119–26. doi: [10.17660/ActaHortic.2014.1017.11](https://doi.org/10.17660/ActaHortic.2014.1017.11).
- König, T., and P. Schreier. 1999. Application of multivariate statistical methods to extend the authenticity control of flavour constituents of apple juice. *Zeitschrift für Lebensmitteluntersuchung und -Forschung A* 208 (2):130–3. doi: [10.1007/s002170050389](https://doi.org/10.1007/s002170050389).
- Kosir, I. J., and M. Kolar. 2010. Use of aromatic profiles as a tool for determining the authenticity of fruit juices. *Hmeljarski Bilten* 17:83–90.
- Kvasnička, F., M. Voldřich, P. Pyš, and I. Vinš. 2002. Determination of isocitric acid in citrus juice—A comparison of HPLC, enzyme set and capillary isotachopheresis methods. *Journal of Food Composition and Analysis* 15 (6):685–91. doi: [10.1006/jfca.2002.1101](https://doi.org/10.1006/jfca.2002.1101).
- Lachenmeier, K., F. Mußhoff, B. Madea, H. Reusch, and D. W. Lachenmeier. 2006. Authentication of noni (*Morinda citrifolia*) juice. *Deutsche Lebensmittel-Rundschau* 102:58–61.
- Le Gall, G., M. Puaud, and L. J. Colquhoun. 2001. Discrimination between orange juice and pulp wash by $(1)\text{H}$ nuclear magnetic resonance spectroscopy: Identification of marker compounds. *Journal of Agricultural and Food Chemistry* 49 (2):580–8. doi: [10.1021/jf001046e](https://doi.org/10.1021/jf001046e).
- Lee, H. S., and R. E. Wrolstad. 1988. Apple juice composition: Sugar, nonvolatile acid, and phenolic profiles. *Journal of the Association of Official Analytical Chemists* 71:789–94.
- Lehnert, N., M. Schmidt, and V. Ara. 2017. Authenticity proof of lemon juices by means of fingerprint methods. *Fruit Processing* 27:314–8.
- Lenhardt, L., R. Bro, I. Zekovic, T. Dramicanin, and M. D. Dramicanin. 2015. Fluorescence spectroscopy coupled with PARAFAC and PLS DA for characterization and classification of honey. *Food Chemistry* 175:284–91. doi: [10.1016/j.foodchem.2014.11.162](https://doi.org/10.1016/j.foodchem.2014.11.162).
- León, L., J. Daniel Kelly, and G. Downey. 2005. Detection of apple juice adulteration using near-infrared transmittance spectroscopy. *Applied Spectroscopy* 59 (5):593–9. doi: [10.1366/0003702053945921](https://doi.org/10.1366/0003702053945921).
- Licciardello, F., G. Muratore, C. Avola, F. Tomaselli, and E. Maccarone. 2011. Geographical origin assessment of orange juices by comparison of free aminoacids distribution. *Acta Horticulturae* 892 (892):389–94. doi: [10.17660/ActaHortic.2011.892.48](https://doi.org/10.17660/ActaHortic.2011.892.48).
- Liu, W., W. Xu, Y. Shang, Q. Linh Trinh, Y. Luo, and K. Huang. 2012. Comparison on the extraction method of DNA and study on the biotechnological detection of orange component in juice. *Journal of Chinese Institute of Food Science and Technology* 12:195–201.
- Louche, L. M. M., E. M. Gaydou, and J. C. Lesage. 1998. Determination of phlorin as peel marker in orange (*Citrus sinensis*) fruits and juices. *Journal of Agricultural and Food Chemistry* 46 (10):4193–7. doi: [10.1021/jf9803637](https://doi.org/10.1021/jf9803637).
- Low, N. H. 1996. Determination of fruit juice authenticity by capillary gas chromatography with flame ionization detection. *Journal of AOAC International* 79 (3):724–37. doi: [10.1093/jaoac/79.3.724](https://doi.org/10.1093/jaoac/79.3.724).
- Low, N. H., A. Brause, and E. Wilhelmsen. 1994. Normative data for commercial pineapple juice from concentrate. *Journal of AOAC International* 77 (4):965–75. doi: [10.1093/jaoac/77.4.965](https://doi.org/10.1093/jaoac/77.4.965).
- Low, N. H., M. McLaughlin, H. J. Hofsommer, and D. A. Hammond. 1999. Capillary gas chromatographic detection of invert sugar in heated, adulterated, and adulterated and heated apple juice concentrates employing the equilibrium method. *Journal of Agricultural and Food Chemistry* 47 (10):4261–6. doi: [10.1021/jf990457w](https://doi.org/10.1021/jf990457w).

- Lubinska-Szczygeł, M., D. Pudlak, T. Dymerski, and J. Namieśnik. 2018. Rapid assessment of the authenticity of limequat fruit using the electronic nose and gas chromatography coupled with mass spectrometry. *Monatshefte für Chemie* 149 (9):1605–14. doi: [10.1007/s00706-018-2242-7](https://doi.org/10.1007/s00706-018-2242-7).
- Magdas, D. A., G. Cristea, R. Puscas, and F. Tusa. 2014. The use of isotope ratios in commercial fruit juices authentication. *Romanian Journal of Physics* 59:355–9.
- Magdas, D. A., A. Dehelean, and R. Puscas. 2012. Isotopic and elemental determination in some Romanian apple fruit juices. *The Scientific World Journal* 2012:1–7. doi: [10.1100/2012/878242](https://doi.org/10.1100/2012/878242).
- Maione, C., E. S. De Paula, M. Gallimberti, B. L. Batista, A. D. Campiglia, F. Barbosa, and R. M. Barbosa. 2016. Comparative study of data mining techniques for the authentication of organic grape juice based on ICP-MS analysis. *Expert Systems with Applications* 49:60–73. doi: [10.1016/j.eswa.2015.11.024](https://doi.org/10.1016/j.eswa.2015.11.024).
- Marieschi, M., A. Torelli, D. Beghé, and R. Bruni. 2016. Authentication of *Punica granatum* L.: Development of SCAR markers for the detection of 10 fruits potentially used in economically motivated adulteration. *Food Chemistry* 202:438–44. doi: [10.1016/j.foodchem.2016.02.011](https://doi.org/10.1016/j.foodchem.2016.02.011).
- Marieschi, M., A. Torelli, and R. Bruni. 2012. Quality control of saffron (*Crocus sativus* L.): Development of SCAR markers for the detection of plant adulterants used as bulking agents. *Journal of Agricultural and Food Chemistry* 60 (44):10998–1004. doi: [10.1021/jf303106r](https://doi.org/10.1021/jf303106r).
- Mauro, A. D., E. Arena, B. Fallico, A. A. Passerini, and E. Maccarone. 2002. Recovery of anthocyanins from pulp wash of pigmented oranges by concentration on resins. *Journal of Agricultural and Food Chemistry* 50 (21):5968–74. doi: [10.1021/jf025645s](https://doi.org/10.1021/jf025645s).
- Medina, S., R. Perestrelo, R. Santos, R. Pereira, and J. S. Camara. 2019. Differential volatile organic compounds signatures of apple juices from Madeira Island according to variety and geographical origin. *Microchemical Journal* 150:104094. doi: [10.1016/j.microc.2019.104094](https://doi.org/10.1016/j.microc.2019.104094).
- Melgarejo, P., D. M. Salazar, and F. Artés. 2000. Organic acids and sugars composition of harvested pomegranate fruits. *European Food Research and Technology* 211 (3):185–90. doi: [10.1007/s002170050021](https://doi.org/10.1007/s002170050021).
- Mooney, R., L. Chappell, and A. I. Knight. 2006. Evaluation of a polymerase chain reaction-based heteroduplex assay for detecting the adulteration of processed orange juice with mandarin juice. *Journal of AOAC International* 89 (4):1052–60. doi: [10.1093/jaoac/89.4.1052](https://doi.org/10.1093/jaoac/89.4.1052).
- Moore, J. C., J. Spink, and M. Lipp. 2012. Development and application of a database of food ingredient fraud and economically motivated adulteration from 1980 to 2010. *Journal of Food Science* 77 (4): R118–R26. doi: [10.1111/j.1750-3841.2012.02657.x](https://doi.org/10.1111/j.1750-3841.2012.02657.x).
- Morin, J.-F., and M. Lees. 2018. *Food Integrity handbook*. Nantes, France: Eurofins Analytics France.
- Moshonas, M. G., and P. E. Shaw. 1994. Quantitative determination of 46 volatile constituents in fresh, unpasteurized orange juices using dynamic headspace gas chromatography. *Journal of Agricultural and Food Chemistry* 42 (7):1525–8. doi: [10.1021/jf00043a025](https://doi.org/10.1021/jf00043a025).
- Mouly, P. P., E. M. Gaydou, and J. Corsetti. 1999. Determination of the geographical origin of Valencia orange juice using carotenoid liquid chromatographic profiles. *Journal of Chromatography A* 844 (1-2):149–59. doi: [10.1016/S0021-9673\(99\)00337-4](https://doi.org/10.1016/S0021-9673(99)00337-4).
- Muntean, E. 2010. Simultaneous carbohydrate chromatography and unsuppressed ion chromatography in detecting fruit juices adulteration. *Chromatographia* 71 (S1):69–74. doi: [10.1365/s10337-010-1598-6](https://doi.org/10.1365/s10337-010-1598-6).
- Murador, D. C., F. Salafia, M. Zoccali, P. L. G. Martins, A. G. Ferreira, P. Dugo, L. Mondello, V. V. de Rosso, and D. Giuffrida. 2019. Green extraction approaches for carotenoids and esters: Characterization of native composition from orange peel. *Antioxidants* 8 (12):613. doi: [10.3390/antiox8120613](https://doi.org/10.3390/antiox8120613).
- Navarro-Pascual-Ahuir, M., M. J. Lerma-García, E. F. Simó-Alfonso, and J. M. Herrero-Martínez. 2015. Quality control of fruit juices by using organic acids determined by capillary zone electrophoresis with poly(vinyl alcohol)-coated bubble cell capillaries. *Food Chemistry* 188:596–603. doi: [10.1016/j.foodchem.2015.05.057](https://doi.org/10.1016/j.foodchem.2015.05.057).
- Ng, C.-C., C.-C. Chang, I. C. Wu, S. Kotwal, and Y.-T. Shyu. 2006. Rapid molecular identification of freshly squeezed and reconstituted orange juice. *International Journal of Food Science and Technology* 41 (6):646–51. doi: [10.1111/j.1365-2621.2006.01125.x](https://doi.org/10.1111/j.1365-2621.2006.01125.x).
- Nikolaou, C., I. K. Karabagias, I. Gatzias, S. Kontakos, A. Badeka, and M. G. Kontominas. 2017. Differentiation of fresh greek orange juice of the merlin cultivar according to geographical origin based on the combination of organic acid and sugar content as well as physico-chemical parameters using chemometrics. *Food Analytical Methods* 10 (7):2217–28. doi: [10.1007/s12161-016-0757-2](https://doi.org/10.1007/s12161-016-0757-2).
- Nisperos-Carriedo, M. O., and P. E. Shaw. 1990. Comparison of volatile flavor components in fresh and processed orange juices. *Journal of Agricultural and Food Chemistry* 38 (4):1048–52. doi: [10.1021/jf00094a029](https://doi.org/10.1021/jf00094a029).
- Obón, J. M., M. C. Díaz-García, and M. R. Castellar. 2011. Red fruit juice quality and authenticity control by HPLC. *Journal of Food Composition and Analysis* 24 (6):760–71. doi: [10.1016/j.jfca.2011.03.012](https://doi.org/10.1016/j.jfca.2011.03.012).
- Pan, M. H., C. S. Lai, and C. T. Ho. 2010. Anti-inflammatory activity of natural dietary flavonoids. *Food & Function* 1 (1):15–31. doi: [10.1039/c0fo00103a](https://doi.org/10.1039/c0fo00103a).
- Panarese, V., L. Laghi, A. Pisi, U. Tylewicz, M. D. Rosa, and P. Rocculi. 2012. Effect of osmotic dehydration on *Actinidia deliciosa* kiwifruit: A combined NMR and ultrastructural study. *Food Chemistry* 132 (4):1706–12. doi: [10.1016/j.foodchem.2011.06.038](https://doi.org/10.1016/j.foodchem.2011.06.038).
- Pardo, M. A. 2015. Evaluation of a dual-probe real time PCR system for detection of mandarin in commercial orange juice. *Food Chemistry* 172:377–84. doi: [10.1016/j.foodchem.2014.09.096](https://doi.org/10.1016/j.foodchem.2014.09.096).
- Perini, M., L. Giongo, M. Grisenti, L. Bontempo, and F. Camin. 2018. Stable isotope ratio analysis of different European raspberries, blackberries, blueberries, currants and strawberries. *Food Chemistry* 239: 48–55. doi: [10.1016/j.foodchem.2017.06.023](https://doi.org/10.1016/j.foodchem.2017.06.023).
- Petrus, D. R., and J. A. Attaway. 1980. Visible and ultraviolet absorption and fluorescence excitation and emission characteristics of Florida orange juice and orange pulp wash: Detection of adulteration. *Journal of AOAC International* 63 (6):1317–31. doi: [10.1093/jaoac/63.6.1317](https://doi.org/10.1093/jaoac/63.6.1317).
- Petrus, D. R., P. J. Fellers, and H. E. Anderson. 1984. Orange juice adulteration: Detection and quality effects of dilution, added orange pulp wash, turmeric and sorbate. *Journal of Food Science* 49 (6): 1438–43. doi: [10.1111/j.1365-2621.1984.tb12816.x](https://doi.org/10.1111/j.1365-2621.1984.tb12816.x).
- Poyrazoğlu, E., V. Gökmen, and N. Artık. 2002. Organic acids and phenolic compounds in pomegranates (*Punica granatum* L.) grown in Turkey. *Journal of Food Composition and Analysis* 15 (5):567–75. doi: [10.1006/jfca.2002.1071](https://doi.org/10.1006/jfca.2002.1071).
- Prusova, P., V. Kruzik, J. Seidl, and H. Cizkova. 2017. Use of electrochemical impedance spectroscopy to verify orange juice authenticity. *Chemické Listy* 111:258–63.
- Pupin, A. M., M. J. Dennis, I. Parker, S. Kelly, T. Bigwood, and M. C. F. Toledo. 1998. Use of isotopic analyses to determine the authenticity of Brazilian orange juice (*Citrus sinensis*). *Journal of Agricultural and Food Chemistry* 46 (4):1369–73. doi: [10.1021/jf970746p](https://doi.org/10.1021/jf970746p).
- Raman, S., O. F. Lange, P. Rossi, M. Tyka, X. Wang, J. Aramini, G. Liu, T. A. Ramelot, A. Eletsky, T. Szyperski, et al. 2010. NMR structure determination for larger proteins using backbone-only data. *Science* 327 (5968):1014–8. doi: [10.1126/science.1183649](https://doi.org/10.1126/science.1183649).
- Rapisarda, P., M. L. Calabretta, G. Romano, and F. Intrigliolo. 2005. Nitrogen metabolism components as a tool to discriminate between organic and conventional citrus fruits. *Journal of Agricultural and Food Chemistry* 53 (7):2664–9. doi: [10.1021/jf048733g](https://doi.org/10.1021/jf048733g).
- Reed, G. H., and C. T. Wittwer. 2004. Sensitivity and specificity of single-nucleotide polymorphism scanning by high-resolution melting analysis. *Clinical Chemistry* 50 (10):1748–54. doi: [10.1373/clinchem.2003.029751](https://doi.org/10.1373/clinchem.2003.029751).
- Reid, L. M., C. P. O'Donnell, and G. Downey. 2006. Recent technological advances for the determination of food authenticity. *Trends in Food Science & Technology* 17 (7):344–53. doi: [10.1016/j.tifs.2006.01.006](https://doi.org/10.1016/j.tifs.2006.01.006).

- Roussel, S., V. Bellon-Maurel, J.-M. Roger, and P. Grenier. 2003. Authenticating white grape must variety with classification models based on aroma sensors, FT-IR and UV spectrometry. *Journal of Food Engineering* 60 (4):407–19. doi: [10.1016/S0260-8774\(03\)00064-5](https://doi.org/10.1016/S0260-8774(03)00064-5).
- Rózańska, A., T. Dymerski, and J. Namieśnik. 2018. Novel analytical method for detection of orange juice adulteration based on ultra-fast gas chromatography. *Monatshefte für Chemie* 149 (9):1615–21. doi: [10.1007/s00706-018-2233-8](https://doi.org/10.1007/s00706-018-2233-8).
- Ruiz Del Castillo, M. L., M. M. Caja, G. P. Blanch, and M. Herraiz. 2003. Enantiomeric distribution of chiral compounds in orange juices according to their geographical origins. *Journal of Food Protection* 66 (8):1448–54. doi: [10.4315/0362-028x-66.8.1448](https://doi.org/10.4315/0362-028x-66.8.1448).
- Ruiz Del Castillo, M. L., M. M. Caja, and M. Herraiz. 2003. Use of the enantiomeric composition for the assessment of the authenticity of fruit beverages. *Journal of Agricultural and Food Chemistry* 51 (5): 1284–8. doi: [10.1021/jf025711q](https://doi.org/10.1021/jf025711q).
- Rummel, S., S. Hoelzl, P. Horn, A. Rossmann, and C. Schlicht. 2010. The combination of stable isotope abundance ratios of H, C, N and S with ⁸⁷Sr/⁸⁶Sr for geographical origin assignment of orange juices. *Food Chemistry* 118 (4):890–900. doi: [10.1016/j.foodchem.2008.05.115](https://doi.org/10.1016/j.foodchem.2008.05.115).
- Saavedra, L., A. García, and C. Barbas. 2000. Development and validation of a capillary electrophoresis method for direct measurement of isocitric, citric, tartaric and malic acids as adulteration markers in orange juice. *Journal of Chromatography. A* 881 (1-2):395–401. doi: [10.1016/S0021-9673\(00\)00258-2](https://doi.org/10.1016/S0021-9673(00)00258-2).
- Saavedra, L., F. J. Rupérez, and C. Barbas. 2001. Capillary electrophoresis for evaluating orange juice authenticity: A study on Spanish oranges. *Journal of Agricultural and Food Chemistry* 49 (1):9–13. doi: [10.1021/jf0004762](https://doi.org/10.1021/jf0004762).
- Schieber, A., P. Keller, and R. Carle. 2001. Determination of phenolic acids and flavonoids of apple and pear by high-performance liquid chromatography. *Journal of Chromatography. A* 910 (2):265–73. doi: [10.1016/S0021-9673\(00\)01217-6](https://doi.org/10.1016/S0021-9673(00)01217-6).
- Scott, M., and A. Knight. 2009. Quantitative PCR analysis for fruit juice authentication using PCR and laboratory-on-a-chip capillary electrophoresis according to the Hardy-Weinberg law. *Journal of Agricultural and Food Chemistry* 57 (11):4545–51. doi: [10.1021/jf9002686](https://doi.org/10.1021/jf9002686).
- Shahidi, F., and P. Ambigaipalan. 2015. Phenolics and polyphenolics in foods, beverages and spices: Antioxidant activity and health effects—A review. *Journal of Functional Foods* 18:820–97. doi: [10.1016/j.jff.2015.06.018](https://doi.org/10.1016/j.jff.2015.06.018).
- Shang, Y., P. Zhu, K. Huang, W. Liu, W. Tian, Y. Luo, and W. Xu. 2014. A peach (*Prunus persica*)-specific gene, Lhcb2, used as an endogenous reference gene for qualitative and real-time quantitative PCR to detect fruit products. *LWT - Food Science and Technology* 55 (1):218–23. doi: [10.1016/j.lwt.2013.08.009](https://doi.org/10.1016/j.lwt.2013.08.009).
- Shaw, P. E., B. S. Buslig, and M. G. Moshonas. 1993. Classification of commercial orange juice types by pattern recognition involving volatile constituents quantified by gas chromatography. *Journal of Agricultural and Food Chemistry* 41 (5):809–13. doi: [10.1021/jf00029a025](https://doi.org/10.1021/jf00029a025).
- Shui, G., and L. P. Leong. 2002. Separation and determination of organic acids and phenolic compounds in fruit juices and drinks by high-performance liquid chromatography. *Journal of Chromatography. A* 977 (1):89–96. doi: [10.1016/S0021-9673\(02\)01345-6](https://doi.org/10.1016/S0021-9673(02)01345-6).
- Sikorska, E., K. Włodarska, and I. Khmelinskii. 2020. Application of multidimensional and conventional fluorescence techniques for classification of beverages originating from various berry fruit. *Methods and Applications in Fluorescence* 8 (1):015006. doi: [10.1088/2050-6120/ab6367](https://doi.org/10.1088/2050-6120/ab6367).
- Simpkins, W. A., G. Patel, P. Collins, M. Harrison, and D. Goldberg. 1999. Oxygen isotope ratios of juice water in Australian oranges and concentrates. *Journal of Agricultural and Food Chemistry* 47 (7): 2606–12. doi: [10.1021/jf981045a](https://doi.org/10.1021/jf981045a).
- Singhal, R. S., P. R. Kulkarni, and R. V. Dinanath. 1997. *Handbook of indices of food quality and authenticity*. Cambridge, UK: Woodhead Publishing.
- Socaci, S. A., C. Socaciu, M. Tofană, I. V. Rați, and A. Pintea. 2013. In-tube extraction and GC-MS analysis of volatile components from wild and cultivated sea buckthorn (*Hippophae rhamnoides* L. ssp. *Carpatica*) berry varieties and juice. *Phytochemical Analysis* 24 (4): 319–28. doi: [10.1002/pca.2413](https://doi.org/10.1002/pca.2413).
- Spinelli, F. R., S. V. Dutra, G. Carnieli, S. Leonardelli, A. P. Drehmer, and R. Vanderlinde. 2016. Detection of addition of apple juice in purple grape juice. *Food Control* 69:1–4. doi: [10.1016/j.foodcont.2016.04.005](https://doi.org/10.1016/j.foodcont.2016.04.005).
- Spraul, M., H. Schäfer, B. Schütz, F. Fang, and M. Link. 2013. Novel NMR-technology to assess food quality and safety. *International Journal of Nutrition and Food Engineering* 7:960–3.
- Spraul, M., B. Schütz, P. Rinke, S. Koswig, E. Humpfer, H. Schäfer, M. Mörtter, F. Fang, U. C. Marx, and A. Minoja. 2009. NMR-based multi parametric quality control of fruit juices: SGF profiling. *Nutrients* 1 (2):148–55. doi: [10.3390/nu1020148](https://doi.org/10.3390/nu1020148).
- Stander, M. A., W. Kühn, and N. F. Hiten. 2013. Survey of South African fruit juices using a fast screening HILIC-MS method. *Food Additives and Contaminants - Part A Chemistry* 30 (9):1473–84. doi: [10.1080/19440049.2013.811545](https://doi.org/10.1080/19440049.2013.811545).
- Statista. 2020. Worldwide juice market. Accessed June 17, 2020. <https://www.statista.com/outlook/20030000/100/juices/worldwide>
- Stöber, P., T. Lamoureux, G. G. Martin, J. M. Durgnat, and C. Hischenhuber. 1998. Standardisation of the detection of invert sugar addition to apple juice by capillary gas chromatography. *Zeitschrift für Lebensmitteluntersuchung und -Forschung A* 207 (4):332–9. doi: [10.1007/s002170050342](https://doi.org/10.1007/s002170050342).
- Stój, A., and Z. Targoński. 2006. Use of amino acid analysis for estimation of berry juice authenticity. *Acta Scientiarum Polonorum Technologia Alimentaria* 5:61–72.
- Subasi, B. G., and H. Alpas. 2017. Effect of high hydrostatic pressure processing and squeezing pressure on some quality properties of pomegranate juice against thermal treatment. *High Pressure Research* 37 (1):78–92. doi: [10.1080/08957959.2016.1263840](https://doi.org/10.1080/08957959.2016.1263840).
- Sun, D. W. 2008. *Modern techniques for food authentication*. Amsterdam, Netherlands: Academic Press.
- Swallow, K. W., N. H. Low, and D. R. Petrus. 2020. Detection of orange juice adulteration with beet medium invert sugar using anion-exchange liquid chromatography with pulsed amperometric detection. *Journal of Association of Official Analytical Chemists* 74: 341–345.
- Thomas, F., C. Randet, A. Gilbert, V. Silvestre, E. Jamin, S. Akoka, G. Remaud, N. Segebarth, and C. Guillou. 2010. Improved characterization of the botanical origin of sugar by carbon-13 SNIF-NMR applied to ethanol. *Journal of Agricultural and Food Chemistry* 58 (22):11580–5. doi: [10.1021/jf102983v](https://doi.org/10.1021/jf102983v).
- Türkyilmaz, M. 2013. Anthocyanin and organic acid profiles of pomegranate (*Punica granatum* L.) juices from registered varieties in Turkey. *International Journal of Food Science and Technology* 48: 2086–95.
- Twohig, M., D. A. Krueger, A. Gledhill, J. Yang, and J. A. Burgess. 2011. Super fruit juice authenticity using multivariate data analysis, high resolution chromatography, UV and Time of Flight MS detection. *Agro Food Industry Hi Tech* 22:23–6.
- Vaclavik, L., A. Schreiber, O. Lacina, T. Cajka, and J. Hajslova. 2012. Liquid chromatography-mass spectrometry-based metabolomics for authenticity assessment of fruit juices. *Metabolomics* 8 (5):793–803. doi: [10.1007/s11306-011-0371-7](https://doi.org/10.1007/s11306-011-0371-7).
- Vaira, S., V. E. Mantovani, J. C. Robles, J. C. Sanchis, and H. C. Goicoechea. 1999. Use of chemometrics: Principal component analysis (PCA) and principal component regression (PCR) for the authentication of orange juice. *Analytical Letters* 32 (15):3131–41. doi: [10.1080/00032719908543031](https://doi.org/10.1080/00032719908543031).
- Vigneau, E., and F. Thomas. 2012. Model calibration and feature selection for orange juice authentication by 1H NMR spectroscopy. *Chemometrics and Intelligent Laboratory Systems* 117:22–30. doi: [10.1016/j.chemolab.2011.05.006](https://doi.org/10.1016/j.chemolab.2011.05.006).

- Vogels, J. T. W. E., L. Terwel, A. C. Tas, F. van den Berg, F. Dukel, and J. van der Greef. 1996. Detection of adulteration in orange juices by a new screening method using proton NMR spectroscopy in combination with pattern recognition techniques. *Journal of Agricultural and Food Chemistry* 44 (1):175–80. doi: [10.1021/jf950062m](https://doi.org/10.1021/jf950062m).
- Wen, L., and R. E. Wrolstad. 2002. Phenolic composition of authentic pineapple juice. *Journal of Food Science* 67 (1):155–63. doi: [10.1111/j.1365-2621.2002.tb11376.x](https://doi.org/10.1111/j.1365-2621.2002.tb11376.x).
- Wiklund, S., E. Johansson, L. Sjöström, E. J. Mellerowicz, U. Edlund, J. P. Shockcor, J. Gottfries, T. Moritz, and J. Trygg. 2008. Visualization of GC/TOF-MS-based metabolomics data for identification of biochemically interesting compounds using OPLS class models. *Analytical Chemistry* 80 (1):115–22. doi: [10.1021/ac0713510](https://doi.org/10.1021/ac0713510).
- Willems, J. L., and N. H. Low. 2014. Authenticity analysis of pear juice employing chromatographic fingerprinting. *Journal of Agricultural and Food Chemistry* 62 (48):11737–47. doi: [10.1021/jf5043618](https://doi.org/10.1021/jf5043618).
- Włodarska, K., I. Khmelinskii, and E. Sikorska. 2018. Authentication of apple juice categories based on multivariate analysis of the synchronous fluorescence spectra. *Food Control* 86:42–9. doi: [10.1016/j.foodcont.2017.11.004](https://doi.org/10.1016/j.foodcont.2017.11.004).
- Wu, H., J. Wang, T. Yue, and Y. Yuan. 2017. Variety-based discrimination of apple juices by an electronic nose and gas chromatography-mass spectrometry. *International Journal of Food Science & Technology* 52 (11):2324–33. doi: [10.1111/ijfs.13514](https://doi.org/10.1111/ijfs.13514).
- Wu, H., T. Yue, and Y. Yuan. 2018. Authenticity tracing of apples according to variety and geographical origin based on electronic nose and electronic tongue. *Food Analytical Methods* 11 (2):522–32. doi: [10.1007/s12161-017-1023-y](https://doi.org/10.1007/s12161-017-1023-y).
- Wu, Y., M. Li, Y. Yang, L. Jiang, M. Liu, B. Wang, and Y. Wang. 2018. Authentication of small berry fruit in fruit products by DNA barcoding method. *Journal of Food Science* 83 (6):1494–504. doi: [10.1111/1750-3841.14177](https://doi.org/10.1111/1750-3841.14177).
- Xu, L., L. Wei, Q. Shi, C. Cai, H.-Y. Fu, and Y.-B. She. 2019. Non-targeted detection of multiple frauds in orange juice using double water-soluble fluorescence quantum dots and chemometrics. *Food Analytical Methods* 12 (11):2614–22. doi: [10.1007/s12161-019-01570-z](https://doi.org/10.1007/s12161-019-01570-z).
- Xu, L., Z. Xu, S. Kelly, and X. Liao. 2020. Integrating untargeted metabolomics and targeted analysis for not from concentrate and from concentrate orange juices discrimination and authentication. *Food Chemistry* 329:127130. doi: [10.1016/j.foodchem.2020.127130](https://doi.org/10.1016/j.foodchem.2020.127130).
- Xu, L., Z. Xu, X. Wang, B. Wang, and X. Liao. 2020. The application of pseudotargeted metabolomics method for fruit juices discrimination. *Food Chemistry* 316:126278. doi: [10.1016/j.foodchem.2020.126278](https://doi.org/10.1016/j.foodchem.2020.126278).
- Xu, W., W. Bai, F. Guo, Y. Luo, Y. Yuan, and K. Huang. 2008. A papaya-specific gene, papain, used as an endogenous reference gene in qualitative and real-time quantitative PCR detection of transgenic papayas. *European Food Research and Technology* 228 (2):301–9. doi: [10.1007/s00217-008-0935-6](https://doi.org/10.1007/s00217-008-0935-6).
- Yang, L., A. Pan, J. Jia, J. Ding, J. Chen, H. Cheng, C. Zhang, and D. Zhang. 2005. Validation of a tomato-specific gene, LAT52, used as an endogenous reference gene in qualitative and real-time quantitative PCR detection of transgenic tomatoes. *Journal of Agricultural and Food Chemistry* 53 (2):183–90. doi: [10.1021/jf0493730](https://doi.org/10.1021/jf0493730).
- Yi, J., B. Jiang, Z. Zhang, X. Liao, Y. Zhang, and X. Hu. 2012. Effect of ultrahigh hydrostatic pressure on the activity and structure of mushroom (*Agaricus bisporus*) polyphenoloxidase. *Journal of Agricultural and Food Chemistry* 60 (2):593–9. doi: [10.1021/jf203405u](https://doi.org/10.1021/jf203405u).
- Zha, H., Y. Cai, Y. Yin, Z. Wang, K. Li, and Z. J. Zhu. 2018. SWATHtoMRM: Development of high-coverage targeted metabolomics method using SWATH technology for biomarker discovery. *Analytical Chemistry* 90 (6):4062–70. doi: [10.1021/acs.analchem.7b05318](https://doi.org/10.1021/acs.analchem.7b05318).
- Zhang, Y., D. Krueger, R. Durst, R. Lee, D. Wang, N. Seeram, and D. Heber. 2009. International multidimensional authenticity specification (IMAS) algorithm for detection of commercial pomegranate juice adulteration. *Journal of Agricultural and Food Chemistry* 57 (6):2550–7. doi: [10.1021/jf803172e](https://doi.org/10.1021/jf803172e).
- Zielinski, A. A. F., C. W. I. Haminiuk, C. A. Nunes, E. Schnitzler, S. M. van Ruth, and D. Granato. 2014. Chemical composition, sensory properties, provenance, and bioactivity of fruit juices as assessed by chemometrics: A critical review and guideline. *Comprehensive Reviews in Food Science and Food Safety* 13 (3): 300–16. doi: [10.1111/1541-4337.12060](https://doi.org/10.1111/1541-4337.12060).