

Review Article

Photodegradation Products and their Analysis in Food

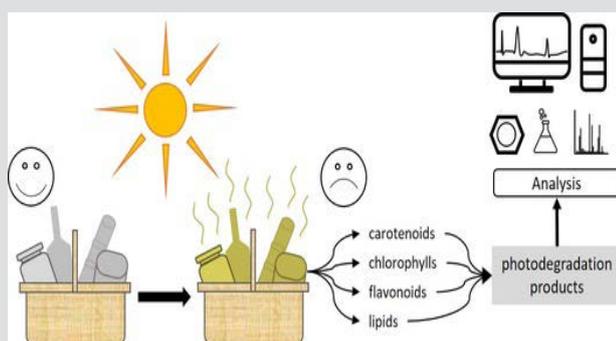
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Graphical Abstract



Abstract

Food spoilage and corresponding waste of packaging material is a serious problem in modern society. Food products can be degraded due to different factors, of which one of them is light-induced degradation. This process can cause the colour of food products to fade or decrease the quality of the product. Moreover, nutrients can be lost or harmful degradation products can be formed. Due to the complex composition of food products, the process of photodegradation is not fully understood and appropriate analysis methods are not fully developed yet. Therefore, this work reviewed

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the photodegradation of different food components (i.e. carotenoids, chlorophylls, flavonoids and lipids) and the analysis of such photodegradation products. The photodegradation reactions involved were found to be photo-oxidation, -isomerisation, hydrogen transfer, hydrogen abstraction and photolysis, with a great variety of photodegradation products. Moreover, the analytical strategies to analyse these in the best possible way were critically reviewed. In general, no other approaches than standard methods have appeared to be used for the analysis of photodegradation studies. (Ultra) high performance liquid chromatography has been found to be the most commonly-used separation technique, with UV and MS as standard detection methods. For specific applications, GC can be used for the separation and unconventional detectors can be used for the detection of the photodegradation species. Examples listed in this review were the electron spray resonance detector for monitoring radical reactions, the vacuum ultraviolet detector for identifying volatiles and high-resolution MS for accurately characterizing the photodegradation species. Using the information and advices given in this review, a better understanding of the nature of the photodegradation species is gained together with strategies to properly analyse these. Nonetheless, due to the complex composition of food products and the influence of other factors than light, more extensive research on this topic still needs to be performed.

Keywords: Chemical analysis; Degradation products; Food spoilage; Photodegradation

Introduction

In modern society, most consumers desire healthy, unprocessed foods without the addition of synthetic compounds. At the same time, they want food to have long shelf-lives, both for their own ease as well as to avoid unnecessary food spoilage. However, the shelf-lives of food products are not infinite, as foodstuffs can degrade, hence spoil, in numerous ways. Generally, there are three ways in which food can spoil: physically, microbially and chemically [1,2]. Factors involved with chemical spoilage are pH, temperature, light and oxygen, of which the latter two are included in the scope of this study. Even though foodstuffs are thermodynamically instable, proper processing and packaging can slow down its degradation [3,4]. Light is one of the factors inducing chemical spoilage of food [1]. Foodstuffs exposed to light can break down into unwanted degradation products. These compounds can cause discolouration and form off-flavours and undesired odours, making the food less appetising [5,6]. Another concern is that photodegradation can decrease the quality of food, for instance by breaking down vitamins and other essential nutrients [7,8]. A simple solution to prevent light-induced degradation of foodstuffs would be the usage of packaging that completely blocks the foodstuffs from all light. Notwithstanding, consumers prefer clear packages so they can see what they buy [6,7]. Thus, in order to protect food from light-degradation and to meet the demands of the consumers, first a proper understanding of the nature of the photodegradation products must be established. However, due to the very complex nature of the composition of foodstuffs, photodegradation pathways of many foods

are challenging to determine. Another problem is that even though there is information available on this topic, it is usually considered as too time-consuming and expensive to perform this type of analysis. Therefore, this review focuses on providing an overview on:

- The different types of photodegradation reactions;
- The nature of the degradation products that are commonly being formed during the photodegradation of food components of interest;
- The analytical strategies to analyse and characterise these degradation products in the best possible way.

Classes of photochemical reactions

There are multiple ways in which molecules can interact with light. When light is being absorbed by a molecule, its energy can either be transferred into heat or induce a chemical reaction [9]. The latter is called a photochemical reaction as it is a reaction that is triggered by light, i.e. a photon is being absorbed to electronically excite a molecule. For this type of reaction to take place, two requirements have to be met:

- The photon energy should be sufficiently high to be absorbed;
- The energy must be high enough to break and form bonds [10]. Photochemical reactions can be divided into two types: direct or photosensitized reactions (Figure 1).

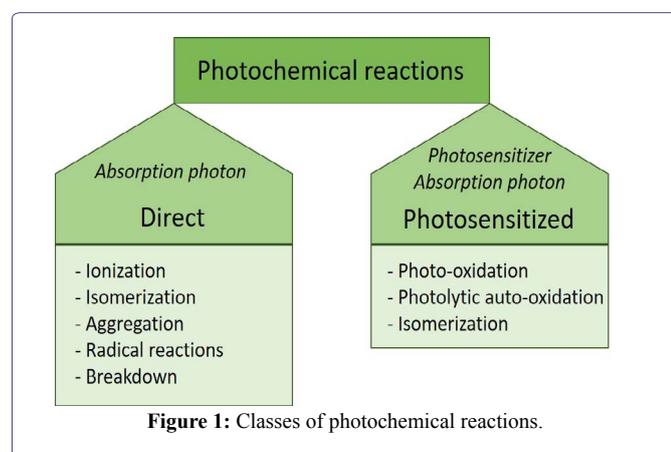


Figure 1: Classes of photochemical reactions.

Direct photochemical reactions

A direct photochemical reaction is a reaction in which a photon is absorbed, inducing a chemical reaction and thereby modifying a molecule [11]. In this type of reaction, light is directly influencing the molecule. The energy of the absorbed photon and the structure of the reacting molecule determines what type of reactions will take place after a direct photochemical reaction. Examples of direct photochemical reactions are ionisation, isomerisation, radical dissociation, aggregation or degradation into other components [10]. Also, secondary reactions can take place via reactive intermediates. These can react further, usually via thermal processes, to form the final reaction product (s).

Photosensitized reactions

In contrast to the direct photochemical reaction, a photosensitized

reaction requires another compound to facilitate the interaction between a molecule with light. Without presence of this so-called photosensitiser, the molecule would not react with light, hence no photochemical reaction would take place [7]. This photosensitiser is a chromophore that contains conjugated double bonds [12]. Photosensitisers are commonly present in foodstuffs, with examples being vitamins and chlorophylls. The electrophilic character of photosensitisers makes them susceptible to different reaction mechanisms, including photo-isomerisation and photo-oxidation (Figure 2).

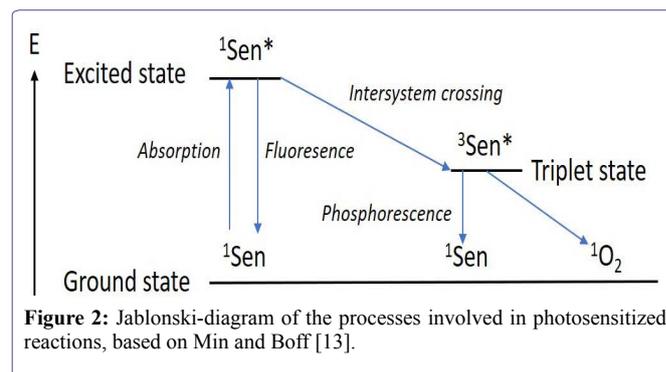


Figure 2: Jablonski-diagram of the processes involved in photosensitized reactions, based on Min and Boff [13].

Photo-oxidation

During photosensitisation, the photosensitiser is first being excited after absorbance of a photon. Then, a photo-oxidation reaction can occur under the presence of oxygen. Naturally, molecular oxygen occurs in the triplet state [14]. However, oxygen can also be formed into the singlet state, in which the antibonding π^* -orbitals are located into one orbital, instead of two separate orbitals. The resulting vacant orbital contributes to the very electrophilic character of this allotrope of oxygen, making it highly reactive towards double bonds [13]. There are various ways in which singlet oxygen can be formed [13]. Photosensitisers can form singlet oxygen under the influence of both oxygen and light [14]. Either visible or UV-light can be absorbed by the sensitiser to form excited singlet sensitiser [13]. The excited singlet sensitiser can either fall back to the ground state via fluorescence, or it can also fall back to a lower energy state via Internal Conversion (IC) (Figure 2) by losing heat. Furthermore, it can be transferred to an excited triplet state via Intersystem Crossing (ISC), after which it can fall back to the ground state via either phosphorescence or by reacting with another compound via type-I or type-II mechanisms (Figure 3).

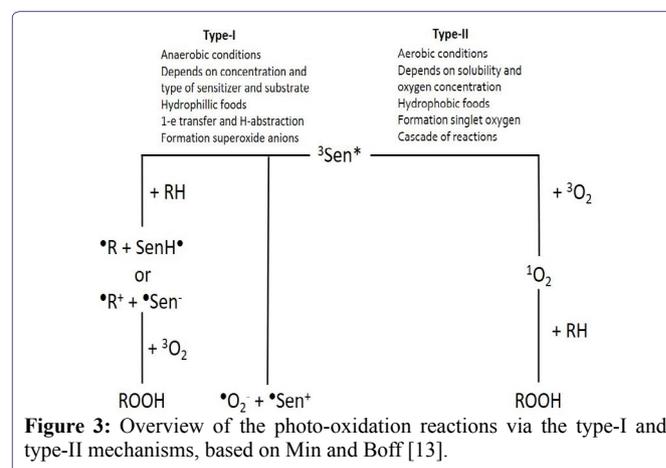


Figure 3: Overview of the photo-oxidation reactions via the type-I and type-II mechanisms, based on Min and Boff [13].

The type-I mechanism occurs more likely under anaerobic conditions [9] and the reaction rate is determined by the concentration and type of the photosensitiser and the substrate [13]. Due to the more hydrophobic nature of oxygen, this type of mechanism occurs more often in hydrophilic food as there is less oxygen present. Examples of food components reacting via the type-I mechanisms include amines and quinones [14]. In the type-I mechanism, one-electron transfer and hydrogen-abstraction are the two reactions caused by the direct interaction between the excited triplet sensitiser and the substrate [6,9]. During H-abstraction, the excited triplet sensitiser donates or accepts H-atoms to induce free radical (chain) reactions [7,14]. During electron transfer, the excited triplet sensitiser reacts with oxygen to form superoxide anions, which occurs in less than 1% of the cases [13]. More often this reaction with oxygen occurs via the type-II mechanism, which is most favourable under aerobic conditions [9]. Since oxygen is better soluble under hydrophobic conditions, the type-II mechanism occurs more often in hydrophobic foods and lipid-water mixtures, such as milk [13]. Its reaction rate is determined by the solubility and the concentration of oxygen in the food. During the type-II mechanism, excited triplet sensitiser can also react with triplet oxygen to form singlet oxygen and singlet sensitiser, which is the dominant (>99%) reaction. The formed singlet oxygen is reactive towards electron-rich compounds, leading to additional reactions of, for instance, double bonds [8]. This results in the formation of hydroperoxides at the place at which the double bond was initially located. This reactive and electrophilic singlet oxygen reacts further with electron-rich compounds to form hydroperoxides. This highly-reactive singlet oxygen reacts with a variety of species to induce degradation, hence decreasing the quality of the food [15].

Photolytic auto-oxidation and photo-isomerisation

Another type of a photo-oxidation reaction is photolytic auto-oxidation, in which lipids are degraded into free radicals due to light exposure [3,14]. The auto-oxidation reactions itself are caused by metal-ions, heat and light that remove a hydrogen atom from a lipid. This leads to formation of free radicals and subsequently hydroperoxide formation [16]. These hydroperoxides further induce free radical chain reactions. Examples of food components that can degrade via this reaction are carotenoids. Carotenoids are very light-sensitive species, so the reaction with atmospheric oxygen occurs rather easily [17]. Besides degrading into different compounds, the molecule can also isomerise into a different conformation via photo-isomerisation. These two reaction mechanisms are in competition with each other and are determined by various parameters, such as the presence of a catalyst, the light intensity and the temperature [18]. An example in food is the all-trans configuration of β -carotene isomerising into different cis-conformations under the presence of light [18,19].

Photodegradation products

The composition of food is complex and the individual ingredients of a food product itself are already difficult to analyse, let alone a mixture of all these compounds. Therefore, this review focuses on a selection of compounds that are commonly present in foodstuffs. Compounds of interest that will be included within the scope of this research are carotenoids, chlorophylls, flavonoids and lipids. Since all these types of compounds are susceptible to light-induced degradation reactions, it is important to understand which type of reactions are involved in each of these compound classes.

Carotenoids

Carotenoids originate from the photosynthetic tissues of microorganisms, plants and algae [17]. These conjugated compounds are very non-polar, meaning that they can be found in hydrophobic parts of a cell, such as the core. Despite its stability towards pH and heat, carotenoids are very light-sensitive due to the electron-rich nature of the chromophore [5]. There are multiple ways in which carotenoids can degrade, including auto-oxidation, thermal degradation, photodegradation and photo-isomerisation, of which the latter two are light-dependent [5,17]. Carotenoids tend to isomerise from the all-trans configuration to different cis-configurations under the influence of heat and light [20]. This isomerisation is not harmful, in fact, it possibly has multiple health benefits. For example, Levin et al. showed that 9-cis β -carotene quenches singlet oxygen in fatty acids better than the all-trans isomer, although no difference in the activity of the two isomers has been found by Liu et al. [21,22]. Moreover, in 2015 Rele-vey et al. showed that the 9-cis isomer could prevent the formation of plaques in arteries [23]. One of the functions of carotenoids in living cells is protecting the cell from DNA and lipid damage from singlet oxygen reactions, meaning that carotenoids function as a quencher for singlet oxygen [17]. Furthermore, carotenoids can also minimise the occurrence of lipid oxidation reactions. In addition, carotenoids can protect organisms, such as plants, against reactions with sensitive species with the so-called inner-filter effect [8]. During the inner-filter effect, light is absorbed by a certain compound, such as a carotenoid, to prevent excitation of another compound [9].

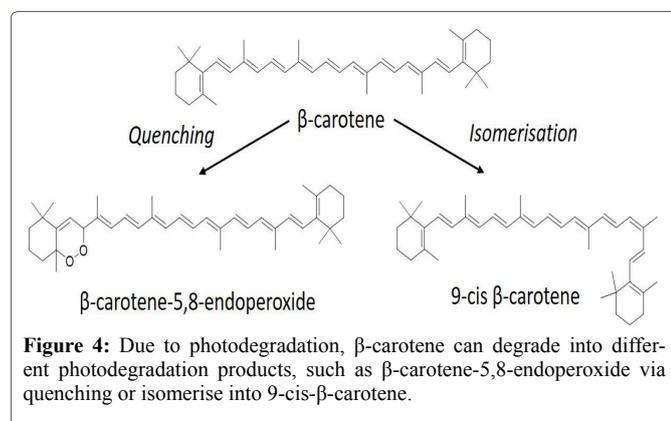
β -carotene

One well-known example of carotenoids is β -carotene. Under the influence of light, β -carotene isomerises from the commonly occurring all-trans configuration to different cis-configurations [18,19]. Besides photo-isomerisation, photodegradation reactions of β -carotene can also occur (Figure 4). For instance, under the influence of light β -carotene can undergo hydrogen-abstraction, forming a β -carotene radical [17]. Moreover, when excited state β -carotene falls back to the ground state, it can undergo reactions with radicals that were formed during the H-abstraction, leading to the formation of β -carotene radical cations. Furthermore, β -carotene can act as a single oxygen quencher [24]. The main degradation product of this quenching reaction is β -carotene-5,8-endoperoxide [8]. Other common degradation products are β -carotene 5,6-epoxide, β -apo-14'-carotenal, β -apo-10'-carotenal, β -apo-8'-carotenal, β -ionone and β -carotenone 5,8-endoperoxide [17]. β -carotene can also protect lipids against light-induced oxidation and it can protect riboflavin from photodegradation with the inner-filter effect [25]. The absorption maxima of β -carotene show that β -carotene can act as a filter against 405 and 436nm. It should be noted that even though exposure of food components at the non-absorbing wavelengths of β -carotene might prevent the photodegradation of the carotenoid itself, it also results in losing the beneficial protecting effects of the carotenoid when it is exposed to non-absorbing wavelengths.

Lycopene

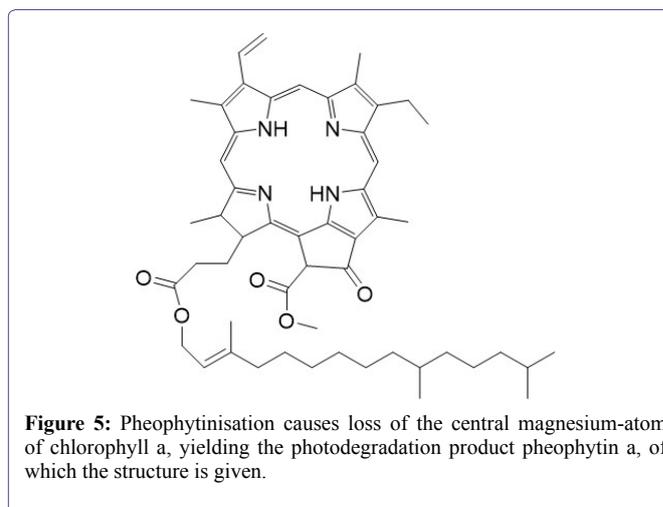
Another frequently abundant carotenoid in foods is lycopene. Just like β -carotene, lycopene can also act as an anti-oxidant and singlet oxygen quencher and its quenching properties are even better than that of β -carotene [26]. The end-groups of β -carotene consist of two closed aromatic rings (Figure 4), whereas these rings are open in the

structure of lycopene. This structural difference was suggested to cause a slower degradation reaction of lycopene [27]. Lycopene also occurs naturally in the all-trans configuration but isomerises into different cis-configurations due to heat, chemical reactions and (visible) light, of which the photo-isomerisation is more probable than the other two causes [26]. During photosensitised oxidation of lycopene, singlet oxygen can be formed. The reaction between singlet oxygen and lycopene leads to formation of a cyclic peroxide [17]. This reactive intermediate can break into degradation products apo-6'-lycopenal and a small amount of oxygenated species. Whereas no safety hazards have been reported for these compounds, the structural difference of these compounds can lead to discolouration or even colour loss.



Chlorophylls

Chlorophylls are involved in the vital process of photosynthesis by absorbing the incoming light [28]. Furthermore, chlorophyll is involved in the charge distribution and electron transport in cellular reactions [29]. As a large variety of food products contain ingredients that are plant-based, chlorophyll is a highly abundant compound in the diet. Its structure is composed of a porphyrin ring with a phytol group and a magnesium ion bound at its centre [30]. This group is non-polar and facilitates the stacking interactions, coordination of metals, and the formation of linear polypyrroles and heteroaromatic rings. Chlorophyll consists of chlorophylls A and B and due to its bright yellow/green colours, chlorophyll is also being used as a food dye. As consumers utilise the vivid green colour as a criterion for good quality, it is important that light degradation of food colorants is prevented to satisfy the demands of consumers. There are multiple factors that can induce degradation of chlorophyll, such as light and the presence of enzymes and micro-organisms [31]. Multiple studies showed that the light-induced degradation of chlorophyll occurs via the process of photo-oxidation [32-34]. Besides chlorophyll A and B, plant-based products can also contain other chlorophyll compounds. For instance, Thron et al. showed that in an olive oil sample both chlorophyll A and B, as well as the degradation product pheophytin were present [34]. This is due to loss of the central magnesium-atom via demetallation or so-called 'pheophytinisation' [35]. The pheophytins are more stable than chlorophyll, however, these itself are susceptible to light, leading to photosensitised oxidations [34]. The study of Thron et al. has also showed that wavelengths below 400nm have a bigger impact on the photosensitised reactions of the chlorophyll derivatives than longer wavelengths. This means that coloured packaging material, green in this example, could be used to filter out damaging wavelength-ranges (Figure 5).



When chlorophyll degrades under the influence of light, it can degrade into red-coloured intermediates, after which its colour can fade completely [32]. This phenomenon is widely being observed during fall, where the leaves transform from green into yellow, orange, red and, ultimately, grey leaves. This is because the oxidation of chlorophyll elongates the conjugated system of chlorophyll, thereby forming phylochromobilins [36]. This formation of red intermediates was also supported by the study by Llewellyn et al., in which was pointed out that the amount of chlorophyll decreased more rapidly than the formation of the colourless end-products [31].

Chlorophyll A

Already in the 1970s, scientists were trying to determine the photo-degradation products of chlorophylls. A study pointed out that photo-oxidation causes the chlorophyll to degrade and that chlorophyll A is degraded via an oxidation at the methine-bridge, since methyl ethyl maleimide was found as a degradation product [32]. At the end of the century, Suzuki et al. found hydrophilic non-coloured compounds and small organic acids as degradation products of chlorophyll A [37]. The proposed reaction was the formation of a monopyrrole intermediate, followed by further degradation via hydrolytic reactions to form hydrolytic monopyrroles and organic acids. Monopyrroles have the risk of acute toxicity so the photodegradation of chlorophyll A might pose health risks, although its concentration in food is probably too low to be harmful [38]. The group of Llewellyn et al. measured no presence of conjugated degradation products, which corresponds with previous results from Suzuki et al. [39]. Similarly, organic acids were found to be the photodegradation products of chlorophyll A. These acids included citric, malonic, succinic and lactic acid and alanine and glycerol. However, it should be noted that both studies were performed in an aqueous environment. In real food samples, the matrix can also be hydrophobic, which could possibly result in different degradation products. A recent study by Petrović et al. from 2017 took into consideration the influence of different types of light on the photodegradation of chlorophyll [35]. Irradiation with white light and UV-B light was compared and it was found that continuous exposure to UV-B light formed the degradation products in a shorter time period than white light. A logical explanation is the higher energy of UV-B light in comparison with that of white light. As described earlier, one of the causes of photodegradation was pheophytinisation. However,

it should be mentioned that this process is not directly caused by light itself, rather than by the biological aging of the chlorophyll. An older research by Heaton et al. in 1996 already showed that other aging processes first degrades chlorophyll into pheorbide molecules, after which these can degrade further under the influence of light and oxygen [40]. This means that the direct degradation by light for chlorophyll is not the only mechanism, but its degradation products formed by different processes could also be sensitive to light. After UV-B irradiation, Petrović et al. detected OH-Pheophytin A (OH-PheoA) and OH-PheoA' as the degradation products of chlorophyll A [35]. Irradiation with visible light showed, in addition to the aforementioned products, formation of OH-lactone-PheoA. Furthermore, studies showed that the irradiation of chlorophyll can lead to the formation of reactive oxygen species, of which the exact mechanisms are still under debate [7,35].

Chlorophyll B

The study by Maunders et al. also showed that, even though chlorophyll B is more light-sensitive than chlorophyll A, the photodegradation of chlorophyll B is slower than that of A [41]. The highly-conjugated structure of chlorophyll makes it a photosensitiser, leading to high reactivity with oxygen species [29,34]. The latter can induce invasive oxidations, which can lead to damaging or even killing cells. When chlorophyll B and lipids are present in the same matrix, the photodegradation of chlorophyll is slowed down [42]. This is probably due to a competition between the two compounds to react with singlet oxygen, of which lipids are more sensitive than chlorophyll B. On the other hand, when chlorophyll is present in a lipid product (vegetable oil), the quality of the product decreased significantly, due to an increased rate of photodegradation of the lipid [43].

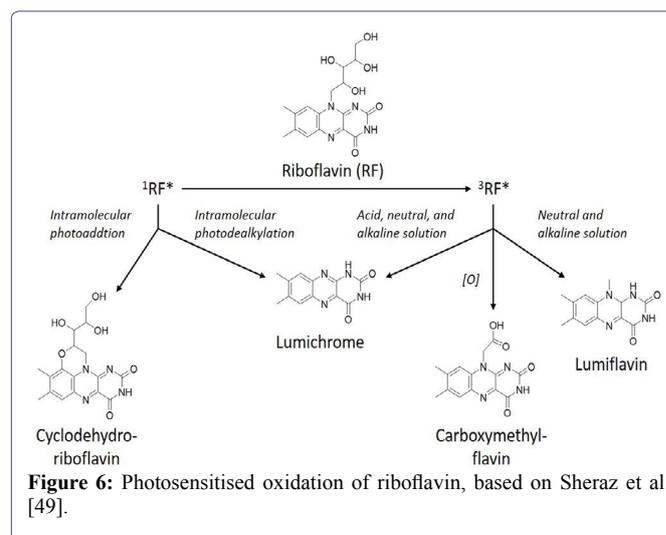
Flavonoids

Flavonoids are a broad group of light-sensitive compounds commonly present in fruits and its structure is composed of a diphenyl propane carbon-skeleton [44]. Due to its strong absorbance between 200 and 380nm, it protects important cellular compounds from ultraviolet radiation, making flavonoids anti-mutagenic, anti-oxidative, and anti-carcinogenic [45,46]. Besides being a healthy food component, flavonoids can also be used as natural food colorants [47]. Considering the molecular structure of these compounds, the presence of highly conjugated systems makes this class very light-sensitive. In fact, photo-oxidation is found to be the main degradation mechanism of flavonoids [7,48]. Flavonoids function as photosensitisers, which means that these compounds can absorb a photon themselves in order to protect other compounds that are present in food [6]. The photo-oxidation can occur either via a type-I or type-II mechanism. For the type-I mechanism, the main degradation products are hydroxyl-peroxyl- and hydroxyl-radicals [6]. For the type-II mechanism, the final degradation products are oxides, hydroperoxides and dioxetanes. The type-I photo-oxidation is caused by H-abstraction, whereas the type-II is initiated by reaction with singlet oxygen [8].

Riboflavin (vitamin B₂)

Riboflavin (vitamin B₂) is a flavonoid that is commonly present in food products, including milk, meat, energy drinks, cheese, white wine and beer [6]. Riboflavin is also known as the hydrophilic vitamin B₂, that is involved in vital processes in the body, for instance by acting as a cofactor in enzymatic reactions and the transfer of

electrons and hydrogen-atoms [49,50]. Besides, the light-absorbing properties of riboflavin were also found to prevent the colour loss of beverages [51]. Already in the 1980s it was known that riboflavin can act as a photosensitiser that degrades due to light [52]. Even earlier, in 1960, Holmström and Oster showed that riboflavin degrades under the influence of visible light and does not necessarily need a photosensitiser to degrade [53]. In the 1990s a study by Bekbölet showed the wavelength-dependent photodegradation of riboflavin, i.e. 450 nm was the most damaging wavelength to riboflavin [24]. Exposed to light, riboflavin can be promoted into the excited triplet state. The excited triplet sensitiser can degrade via either type-I or type-II photosensitisation. Due to the type-I degradation, radicals can be formed that can react with riboflavin to form the degradation products lumichrome, lumiflavin and hydroxyl radicals [7]. With the type-II mechanism, singlet oxygen reacts with riboflavin to form degradation products. This breakdown of riboflavin reduces the positive health effects of the flavonoid. The photodegradation mechanism has been explored quite thoroughly in earlier studies and Sheraz et al. proposed a general scheme of the photodegradation pathway of riboflavin [49] (Figure 6).



Photoreduction, -addition and -dealkylation were described as the main degradation mechanisms for both inter- and intramolecular reactions of riboflavin [49]. The photodegradation products are formylmethylflavin, lumichrome, lumiflavine, carboxymethylflavin, 2,3-butanedione, and cyclodehydroriboflavin. Furthermore, the pH affected the final degradation products. At a higher pH, also diketone-compounds and beta-keto acids were formed via alkaline hydrolysis [54]. Riboflavin was proven to be less stable at low pH [55]. This could be the cause of better scavenging of radical species at a high pH, as demonstrated by a study by Barua et al., in which the anti-oxidising properties of the flavan-3-ol (+)-catechin were more efficient at low pH [56]. Of all the detected degradation products, the only one with health risks is 2,3-butanedione as it can cause acute toxicity [57]. Besides pH-dependence, the presence of oxygen also determines the degradation pathway, as aerobic conditions favour type-I mechanisms. Therefore, the intramolecular photo reduction occurs under anaerobic conditions and leads to fading of the colour [53,58].

This process is not necessarily irreversible and thus could be reversed after addition of oxygen. Besides colour loss, riboflavin also loses its dietary benefits while gaining off-flavours [55]. Nonetheless, food products are composed of a great number of different compounds. Thus, it is not unthinkable that other compounds present in the food matrix could prevent certain degradation mechanisms from occurring. For example, when both riboflavin and carotenoids are present in a food product, the carotenoid can prevent riboflavin-sensitised oxidation with the inner-filter effect [9]. In this way, no excited triplet state riboflavin can be formed. Furthermore, another important parameter to consider is the wavelength at which the product is exposed. Sheraz et al. showed that the degradation of riboflavin was faster under ultraviolet than visible light [49]. The same trend was also observed in the degradation of chlorophylls [35].

Flavonols, flavanones, flavanols and flavones

Flavonols find their origins in fruits and vegetables and vivid green leaves are rich in flavonols [59]. Flavonols have anti-oxidising properties and can protect against ultraviolet radiation. Studies investigating the flavonol quercetin have shown that the absorbance of UV-A and UV-C light prevent the formation of reactive oxygen species, thereby preventing DNA-damage. The absorbance of these types of light can also prevent liposome peroxidation by UV-C light and reduce skin damage by UV-B light. Excited-state intramolecular hydrogen transfer induces photodegradation of flavon-3-ols and subsequent relaxation releases energy in the form of heat [6]. Known photodegradation products of quercetin under the influence of UV-A and UV-B light are listed in table 1 [59]. Flavanols, compounds commonly present in tea, are capable of quenching singlet oxygen [8]. 4-hydroxy benzoic acid was found to be one of the final photodegradation product of flavanols and flavanones. The quenching properties of flavanols have also proven to be pH-dependent. For instance, the flavan-3-ol (+)-catechin was a more efficient scavenger at high pH [56]. This means that the anti-oxidising properties can be less powerful in acidic foodstuffs, such as sodas and dairy-products, causing these products to be more light-sensitive. The most efficient anti-oxidisers within the group of flavonoids are the flavones. They originate from flowers, leaves and fruits [46]. The flavone apigenin is proven to protect against UV-A and UV-B light and thereby preventing the reactions with reactive oxygen species [59]. Remarkably, studies showed that photodegradation of flavones is faster in polar solvents than in non-polar solvents [45,60]. This suggests that a type-I photosensitised degradation mechanism is favoured, which is more probable in a hydrophilic environment. A recent study by Chaaban et al. detected four degradation products for the flavone eridictyol [61]. Unfortunately, the structure of these degradation products was not characterised and the exact reaction mechanism is still unknown.

Isoflavones

The main source of isoflavones is soy [6]. Examples of isoflavones are genistein, daidzein and glycitein [8]. Riboflavin activity can increase the activity of anti-oxidants in these isoflavones-compounds. Hydrogen abstraction and reactions with singlet oxygen are the causes of photodegradation of daidzein. 3'-hydroxydaidzein and two dimers were found to be the main degradation products [63]. The other common isoflavone, genistein, functions as an anti-oxidant by aiding anti-oxidant enzymes, scavenging free radicals and by blocking UV-A and UV-B radiation [59].

Anthocyanins and anthocyanidins

The final types of flavonoids that will be considered in this section are the anthocyanins and anthocyanidins. These group of flavonoids cause the vivid colours in brightly-coloured fruits, such as strawberries, blackberries, blueberries, grapes and avocado's as well as in eggplant [6]. Anthocyanins are unstable compounds that are sensitive towards many factors, including the presence of other compounds, enzymes, pH, temperature, as well as light and oxygen [68]. The colour is pH-dependent and can range from red at low pH-values and purple and blue colour at pH-values above 6 [30]. Since food products usually have a mild pH, the anthocyanins are mostly red-coloured or even colourless. Anthocyanins and -cyanidins can protect plant structures that play a role in photosynthesis against light irradiation by absorbing ultraviolet light and blue and green light [6,69]. However, for this protection, anthocyanins need to bind or interact to another compound to form a stable complex [8]. Instead of absorbing light, anthocyanins can also transfer light into heat by deactivating the excited triplet state [6]. Besides functioning as reactive oxygen species scavengers, anthocyanins can also chelate with metals to prevent toxic metal concentrations leading to complications in plants [70]. A recent study by Chen et al. reported that temperature had a higher impact on the degradation of anthocyanins than light [71]. Anthocyanidins can also protect plants by converting the excited states back to the ground state while releasing the excess energy as harmless heat [8]. Due to their instability, other compounds, such as peptides, amino acids or phenolic compounds, must be present in the matrix to prevent anthocyanidins from degrading. Chalcone was found to be the photodegradation product, as well as the thermal degradation product of the anthocyanide malvidin [64]. This compound is toxic, so the photodegradation of anthocyanidins not only leads to colour fading or colour loss, but it could also pose health risks to the consumer, although that might be negligible at the low concentrations present in foodstuffs. Furthermore, in real life, anthocyanins are not the only compound present in the food matrix. In many foodstuffs, ascorbic acid (vitamin C) is present in the product. It was already proven that ascorbic acid influences the photodegradation of other compounds, including anthocyanins [5,72]. A recent publication by Gérard et al. demonstrated the effect of ascorbic acid on the colour loss of anthocyanins in different plant extracts [73]. This study showed that anthocyanins alone were less stable in air than in a nitrogen atmosphere, whereas they became more stable in air than in nitrogen atmosphere when ascorbic acid was present. An explanation for this is that when anthocyanins are exposed to light, peroxy-radicals can be formed under aerobic conditions. However, addition of ascorbic acid could prevent peroxidation from happening via hydrogen transfer, explaining the protecting properties of ascorbic acid under aerobic conditions.

Lipids

Another class of compounds to be considered are lipids. Lipids can degrade in numerous ways under the influence of light via lipid oxidation and the rate of oxidation is increased due to microbial spoilage and the presence of ultraviolet light [11,74]. When lipids are exposed to light, the volatile degradation products lead to off-flavours and off-odours [7]. Moreover, the formation of harmful degradation products poses a danger regarding human health [16]. Therefore, it is utterly important that the degradation products of lipids are discussed, especially regarding the fact that lipids are abundant in food.

Compound	Photodegradation Reaction	Photodegradation Product	Reference
Carotenoids β-carotene	Photo-isomerisation H-abstraction Singlet oxygen quenching, inner filter effect	Cis-isomers (9-cis main isomer) β-carotene radical, β-carotene radical cations β-carotene-5,8-endoperoxide, β-carotene 5,6-epoxide, β-apo-14'-carotenal, β-apo-10'-carotenal, β-apo-8'-carotenal, β-ionone	[18-20,26] [62] [8,17,24]
Lycopene	Photo-isomerisation Photosensitized oxidation	Cis-isomers Apo-6'-lycopenal and oxygenated species	[26] [17]
Chlorophylls Chlorophyll A	Photo-oxidation Hydrolytic reactions	Methyl ethyl maleimide, hydrolytic monopyrroles, organic acids Organic acids (lactic, citric, succinic and malonic acid), alanine and glycerol OH-Pheo α and OH-Pheo α' and OH-lactone-Pheo α (only in visible light) Organic acids, hydrolytic monopyrroles	[32] [31,37] [35] [7,32,35]
Flavonoids Riboflavin (vitamin B ₂)	Photo-oxidation Alkaline hydrolysis	Lumichrome, lumiflavin and hydroxyl radicals, formylmethylflavin, lumichrome, lumiflavine, carboxymethylflavin, 2,3-butanedione and cyclodehydroriboflavin Diketo compounds and β-keto acid	[7,49] [54]
Quercetin	Hydrogen transfer	2,4,6-trihydroxybenzaldehyde, 2-(3'-4'-dihydroxybenzoyloxy)-4,6-dihydroxybenzoic acid and 3,4-dihydroxyphenyl-ethanol	[59]
Flavanone and flavanol	Photo-oxidation	4-hydroxy benzoic acid	[8]
Isoflavonoids	Photo-oxidation	3'-hydroxydaidzein	[63]
Anthocyanidins	Photo-oxidation	Chalcone	[64]
Lipids Linoleic acid	H-abstraction	9-10E 12Z-LAOOH, 9-10E 12E-LAOOH, 10-8E 12Z-LAOOH, 12-9Z 13E-LAOOH, 13-9Z 11E-LAOOH and 13-9E 11E-LAOOH	[15,65]
Linoleic acid ethyl ester	H-abstraction	9-10E 12Z-ELAOOH, 9-10E 12E-ELAOOH, 10-8E 12Z-ELAOOH, 12-9Z 13E-ELAOOH, 13-9Z 11E-ELAOOH and 13-9E 11E-ELAOOH	[15,65]
Phytosterols Ergosterol	Photo-oxidation, photosensitized oxidation (accelerated degradation) Photo-oxidation	7β-hydroxy (main), 7α-hydroxy, 5β,6β-epoxy, 7-keto, 5α,6α epoxy and 6β-hydroxy Lumisterols, tachysterols and previtamin D ₂	[8,66] [67]

Table 1: Overview of the photodegradation reactions and corresponding degradation products per compound class.

The photodegradation of lipids occurs via the process of photo-oxidation, which is a type of photosensitized degradation. Fatty acids, the main components of vegetable oils, can separately not absorb light when the wavelength is lower than 220nm [16]. Moreover, the sensitivity of lipids towards light can be explained via the nature of photodegradation itself. Oxygen is more soluble in hydrophobic matrices, making the light-sensitive properties of lipids a very logical phenomenon. When hydrogen peroxide is formed, it can react further into hydroxy radicals, which are reactive species that can initiate a cascade of radical reactions [62]. The peroxide radical is particularly reactive towards electrophiles, meaning that double-bond containing compounds, such as unsaturated fatty acids, are very sensitive for this radical-based degradation. The resulting oxidation reactions would lead to the formation of peroxides, which could cause rancidity in food products such as vegetable oil and meat [6,75]. However, real lipid products are not only composed of fatty acids, but other compounds as well. These compounds could influence the degradation. Likewise, anti-oxidants can prevent lipids from degrading by:

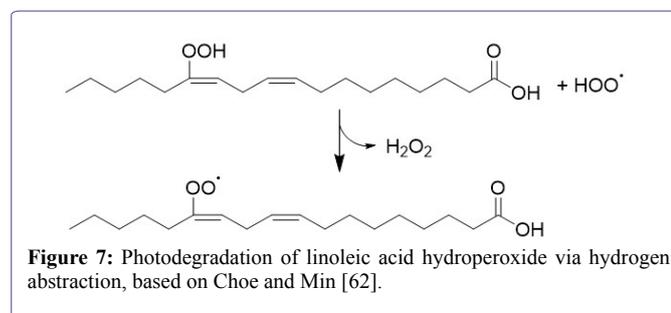
- Reacting with free radicals; or
- By decreasing the formation of hydroperoxides [75].

Fatty acids

As mentioned before, one of the components of fats are fatty acids. Vegetable oils are mainly composed of triglycerides, which are triacylglycerols that are made from three fatty acids. Oils can be degraded into hydroperoxides under the influence of multiple factors, including the presence of catalysts, heat, oxygen and light. The instability of these hydroperoxides leads to further degradation into a large variety

of degradation products, such as lactones, carboxylic acids, ketones, alcohols and acids [16,76]. Spataro et al. compared different types of vegetable oil (i.e. soybean, olive, corn, linseed, sunflower and corn oil) on light-sensitivity [76]. As expected, the fatty acid (linoleic and oleic acid) contents decreased when the vegetable oils were exposed to light. Unfortunately, the degradation products of these oils were not discussed, but remarkable is the difference between the extent of photodegradation between the different oils. For instance, olive oil was proven to be the most light-stable oil, whereas soybean and sunflower oil were demonstrated to be very light-sensitive. Possibly the presence of many polyunsaturated fatty acids in soybean makes it more reactive towards light in comparison with the other oils. As corn oil also contains a considerable amount of fatty acids, the same trend as for soybean oil would have been expected. However, corn oil was clearly more stable towards light than sunflower oil. Peanut oil and sunflower oil were both rich in vitamin E that should function as an anti-oxidant [7], so the expectation would be that these oils would be less light-sensitive than the other oils that lack vitamin E. However, no further explanation for this explanation has been given by Spataro et al., hence this must be studied more thoroughly. This example illustrates that the composition of food, which is very complex, influences the photodegradation. Linoleic Acid (LA) and its Ethyl Ester (ELA) are two compounds that are commonly present in food products and cosmetics [65]. In 2019, Ito et al. performed a detailed study on the photodegradation of these compounds and a large variety of hydroperoxide isomers were found to be the photo-oxidation products, including linoleic acid and ethyl ester hydroperoxides (LAOOH and ELAOOH, respectively). Choe and Min already described the reaction mechanism of this degradation of linoleic acid in 2005 [62]. The

oxidation occurs via the reaction between a hydroxy radical and linoleic acid via hydrogen abstraction (Figure 7). This radical can either abstract a hydrogen-atom from the lipid to form lipid radicals or a hydrogen-atom from lipid hydroperoxides to form peroxy radicals.



As displayed in table 1, photodegradation of linoleic acid yielded six isomers and the light-induced degradation of linoleic acid ethyl ester yielded six other isomers [65]. The results by Ito et al. showed how sensitive the fatty acids are towards light and oxygen, as these degradation products were already being formed during the processing of the product. Moreover, the formation of the hydroperoxides induces formation of off-flavours and off-odours, decreasing the appearance, flavour, hence the quality of the product.

Sterols

Besides fatty acids, other lipids can be present in foodstuffs as well. For instance, phytosterols are sterol molecules that are chemically similar to cholesterol [77]. Phytosterols are being used as additives in food products and because of its structural similarities with cholesterol, these could be beneficial for individuals that have high levels of cholesterol [78]. Phytosterols are sensitive to many factors, such as oxygen, heat, lipid matrix, the presence of transition metals and light [66]. The photo-degradation was demonstrated to occur faster when photosensitisers were present in the matrix. Similar results were obtained by Li et al. in 2019 [43]. Just as other lipids, phytosterols are degraded via photo-oxidation under the presence of light. For a long time, the exact reaction mechanism was not known yet, until Zhao et al. proposed the photo-oxidation reactions in detail in 2019 [66]. The corresponding photodegradation products included 7 β -hydroxy, 7 α -hydroxy, 5 β ,6 β -epoxy, 7-keto, 5 α ,6 α epoxy and 6 β -hydroxy, of which 7 β -hydroxy was the main product. In 2017, similar degradation products under the influence of sunlight and UV-light were described [8]. Moreover, it is noteworthy to mention that the thermal degradation products that Lin et al. have described were the same as the photodegradation products, suggesting that thermal and photodegradation might yield the same products [79]. Safety risks of these compounds have not been reported, however the decomposition of the phytosterols into smaller degradation products leads to functionality loss of the sterols.

Ergosterol is a type of phytosterol that poses positive health effects when it is degraded by light [8]. Under the influence of UV-light, ergosterol degraded into multiple compounds, such as lumisterols, tachysterols and previtamin D₂, of which all could be transformed into vitamins D [67]. Therefore, it can be used as a supplement for vitamin D. This example shows that the photodegradation of food compounds does not always negatively influence human health. Especially regarding the fact that the majority of the population has a

vitamin D-deficiency, the photodegradation of ergosterol could be beneficial to restrain this problem [80]. Unfortunately, another degradation product, tachysterol, was reported as toxic, hence the overall health benefit was compromised [81].

The analysis of photodegradation products

Now that the general photodegradation reactions of the compound classes are understood, methods for the analysis of photodegradation species will be critically discussed. An overview of all analytical methods that were described in the literature for the analysis of photodegradation products in food are given in Table 2.

Sample preparation

Sample preparation is key for accurate characterisation of photodegradation products. During the pre-treatment step, the analytes of interest must be extracted from the matrix in a correct manner. Insufficient extraction of the analytes could lead to underestimation of the levels of certain compounds in food or inability to detect certain species and improper treatment of the sample could lead to degradation of the sample. In the latter case, a sample would not only be degraded by light but by the stress of the extraction method as well. When the aim is to study the photodegradation of food compounds, it is important that other factors that could induce degradation are excluded. For instance, besides light-degradation, compounds can also degrade via pH-differences and heat. Especially regarding the fact that some studies suggest that thermal and photodegradation yield the same products, it is important to carefully perform the sample preparation [64,79]. Since the matrix of the product determines the type of sample treatment, this section will be divided into different subsections in which suitable preparation steps will be described per type of food product.

Beverages

Generally, minimal sample preparation is needed when analysing beverages. Common pre-treatments include (liquid-liquid) extraction, filtration and occasionally homogenisation. Another type of sample preparation that has been found for the analysis of beverages is buffering to change the pH [73]. However, the operator must be careful when changing the pH as it can degrade food components such as the food dyes carminic acid and gardenia blue [7,85]. Moreover, the pH can also influence what type of degradation products will be formed, as shown by the study of Ahmad et al. [54]. As the pH in various food products can be different, it might be interesting to determine the degradation products under different pH-conditions. In this way, the type of photodegradation products that are present in different food matrices with specific pH-values could be predicted.

Fruits and vegetables

In most fruit and vegetable samples, the first step is homogenisation of the product. Traditionally, the first step is performed using a blender. However, during blending heat is being formed that can induce thermal degradation. In that way, not solely the photodegradation products cannot be separated from the thermal degradation products. Therefore, nowadays, freeze-drying is a more common method to homogenise the sample. In that way, no heat is being formed, which reduces the risk of degrading the product by other factors than light. Following homogenisation, the sample can be filtered and/or centrifuged to remove solids.

Compound Class	Product	Sample Preparation	Separation Technique	Detection Technique	Year	Reference
Carotenoids						
α - and β -carotene and lycopene	Vegetable juice	Extraction, filtration (cheese-cloth)	RPLC C ₁₈ (4.5 x 250mm, 5 μ m)	UV (variable wavelength)	1987	[27]
β -carotene	Standards	Dissolution, filtration (membrane filter)	RPLC C ₁₈ (4.6 x 250mm, 5 μ m)	PDA (450nm for β -carotene, 600 nm for chlorophyll a)	1998	[19]
Lycopene	Tomatoes	Homogenisation (blender), extraction	RPLC polymeric C ₃₀ (4.6 x 250mm, 3 μ m)	DAD (472nm)	2003	[26]
Chlorophylls						
Chlorophyll A/B		[82]	TLC GC	MS, NMR	1970	[32]
Chlorophyll A/B	Plant material	Homogenisation, filtration (cotton), centrifugation	RPLC with ion pair C ₁₈ (25cm, 5 μ m) IEC divinylbenzene resin (30cm)	UV (210nm)	1974 1990	[31,83]
Chlorophyll	Plant material	Dissolution, centrifugation, extraction	TLC	Spectrophotometer	1983	[41]
Chlorophyllin	Standards	- Dissolution, extraction Acidification, extraction	- - RPLC C ₁₈ (4.6 x 250mm, 10 μ m)	IR Cyclic voltammetry MS (quadrupole ion trap)	1999	[33]
Chlorophyll A	Radish seedlings, barley	Extraction	RPLC ODP-50 (4.6 x 250mm)	Spectrophotometer (280nm)	1999	[37]
Chlorophyll	Standards in sunflower oil	Headspace	- GC	DAD FID	2001	[34]
Chlorophyll B	Standards in paraffin oil and triglycerides	Dissolution	RPLC C ₁₈ (4.6 x 250mm, 5 μ m)	UV/Vis (438nm)	2014	[42]
Chlorophyll B	Spinach	Homogenisation (grinding), extraction, centrifugation, filtration Extraction (open column chromatography)	RPLC (UHPLC), C ₁₈ (2.1 x 50mm, 1.9 μ m)	DAD (380, 407, 430, 660nm) MS (ion trap)	2017	[35,84]
Chlorophyll	Chlorophyll-spiked rapeseed oil		-	UV (620-720 nm)	2019	(Li et al. 2019) [43]
Flavonoids						
Flavones	Standards	Dissolution	RPLC C ₁₈ (4 x 125mm, 5 μ m)	UV (190-400nm)	1993	[45]
Anthocyanidin	Standards	-	RPLC C ₈ (4.6 x 250mm, 5 μ m)	UV (280nm)	1993	[64]
Riboflavin (vitamin B ₂)	Standards	-	TLC	UV (365nm) Spectrophotometer (240nm)	2004	[54]
Riboflavin (vitamin B ₂)	Standards	Dissolution	RPLC C ₁₈ (3.9 x 150mm) RPLC C ₁₈ (3.9 x 150mm)	UV/Vis (260nm) MS (Quadrupole)	2010	[63]
Riboflavin (vitamin B ₂)	Milk	Centrifugation, ultrafiltration	RPLC ODS (3 x 100mm, 3 μ m) RPLC (UHPLC) HSS T3 (2.1 x 150mm, 1.8 μ m)	Fluorescence (420nm excitation, 530nm emission) MS (HR)	2018	[55]
Anthocyanin	Sweet potato (purple)	Homogenization (freeze drying and milling), extraction pH alternation Dissolution	- - -	UV/Vis (525, 700nm) Colorimeter Spectrophotometer (517nm)	2019	[71]
Anthocyanin	Carrot (black)/grape juice/sweet potato (purple) extracts in beverages	Buffering Dissolution (and degassing) Dissolution	- - -	UV/Vis (200-700nm) Cyclic voltammetry ESR Fluorimeter	2019	[73]
Lipids						
General	Vegetable oils	Dissolution, extraction, acidification	RPLC C ₁₈ (4.6 x 250mm)	DAD	2016	[76]
Linoleic acid and linoleic ethyl ester	Standards Liquor	Dissolution	- RPLC ODS-3 (2.1 x 150mm, 5 μ m) (LAOOH) RPLC C ₁₈ (2.1 x 150mm, 5 μ m) (ELAOOH)	¹ H-NMR (400 MHz) MS (Quadrupole ion trap) MS (Quadrupole ion trap)	2019	[65]
Phytosterol	Standards	Dissolution, saponification, incubation, SPE	GC	MS (Not specified)	2019	[66]

Table 2: Overview of the analytical methods used to analyse photodegradation products of the compounds of interest.

During these steps, part of the analyte can get trapped onto the filter/precipitate resulting in a lower recovery of the analyte. When the sample is spiked with a representative standard, the analyte loss can be estimated. This can be used to correct the detected values when quantitative analysis is desired. Besides filtration and centrifugation, changing the pH can be another step, of which the disadvantages have already been described. The final step in the sample preparation of plant material is extraction of the analyte. Liquid-Liquid Extraction (LLE) was the most common type of extraction that was found in the studied literature. Another type of extraction that can be used is open-column chromatography, which has been used by Petrović et al. in 2017 [35]. During their analysis, the open column contained silica particles, meaning that the principle is similar to Solid-Phase Extraction (SPE). Both open-column chromatography and SPE could be useful as a sample clean-up step as it can retain the interfering compounds on the silica, rather than the analyte. In contrast to LLE, SPE can be performed on-line. When (part of) the sample preparation can be performed on-line along with the analysis, the overall method becomes more efficient: it saves time, automation is possible, it reduces errors by the operator, and it might even minimise the risk of degradation during the off-line sample preparation. However, suitable sorbents must be available to realise this.

Oils and fats

In line with beverages, sample preparation of oils is less difficult than for solid samples as the analyte is already present in a liquid matrix. As table 2 shows, not all samples needed extensive sample preparation before analysis. For instance, when only UV-detection was performed, the product could be analysed directly. Similarly, when High-Performance Liquid Chromatography (HPLC) was used as a separation technique, sample preparation was not necessarily needed as HPLC can also separate the analyte from the other components. When Gas Chromatography (GC) is desired, head-space extraction could be performed to extract volatile analytes while transferring it into the gaseous phase. These given examples all have the advantage that these are compatible with an on-line system. However, more extensive sample preparation might be needed as well. For instance, Spatari et al. used saponification to hydrolyse the triglycerides to separate the different kind of fatty acids [76]. This procedure is not easy to automate and therefore time-consuming. Another type of food product with high levels of fat is milk, which is an emulsion of fat and water. The sample preparation for milk is also more difficult than for vegetable oils. Fracassetti et al. prepared milk samples by first centrifugation and subsequent ultra filtration of the bottom layer, followed by filtration [55]. In contrast to the saponification procedure, the method by Fracassetti et al. is less labour-intensive. These examples illustrate that the sample preparation of oils is not necessarily difficult, but the type of treatment depends on the product and the type of analysis.

It can be concluded that the sample preparation is an important step in the analysis of food products and one should take care to develop a method that is non-destructive towards the analyte. Different circumstances, (e.g. pH, solvent and external factors such as heat formation) can be tested during the degradation studies of standards to understand how compounds degrade in different matrices. It is suggested to first start analysing the standard on its own, after which combinations of two or more food components can be tested. This can be used to predict the type of degradation products that will be

formed after light-illumination of real food products, which are mixtures of different compounds. Depending on the analyte and the type of matrix, even on-line coupling of sample preparation steps, such as headspace and SPE, can be possible, making the degradation studies less time-consuming and easy to automate. Such an on-line system would be especially useful for routine analysis in industry.

Separation

The techniques used for the separation of the photodegradation products from carotenoids, chlorophylls, flavonoids and lipids are enlisted in table 2. Since this table already gives an overview of all techniques found in the cited literature, only the trends and critical remarks will be given in the next section to show which techniques are useful for the analysis of photodegradation products.

Carotenoids

HPLC was used as a separation technique in all studies that have been investigated in this review. Either a silica C_{18} -column or a polymeric C_{30} -column was used for the separation for the degradation species of carotenoids. Comparison of a C_{30} -column with C_{18} -columns showed that the latter are suitable for the analysis of the more hydrophobic carotenoids, flavonoids, phenolic acids and isomers [86]. The C_{30} -columns are suited for distinguishing the cis-isomer degradation products from carotenoids. However, Turcsi et al. emphasised that this isomeric separation power comes with the cost of poor separation of polar carotene-species [87]. Thus, it is advised to use C_{18} -columns for the general analysis of photodegradation products of carotenoids and to use polymeric C_{30} -columns for the specific analysis of long-chain hydrophobic photo-isomerisation products.

Chlorophylls

Chlorophyll has been analysed for over several decades and in earlier days Thin Layer Chromatography (TLC) and GC have been used as separation techniques [34,41,82]. Nowadays, Reversed Phase Liquid Chromatography (RPLC) is the most commonly used technique for the analysis of chlorophylls. A conventional LC-mode is RPLC using a silica C_{18} -column. When analysing food components in solvents with extreme pH-values, regular C_{18} -columns might not be resistant against these conditions, hence the use of polymeric columns can be advantageous over regular C_{18} -packings. Moreover, also modified RPLC, such as ion-pair RPLC or even Ion Exchange Chromatography (IEC) can be used to analyse the degradation products of chlorophyll (Llewellyn et al. 1990a). These methods could be more suitable for the analysis of relatively polar photodegradation products, such as the organic acids that are formed after the photodegradation of chlorophyll A, as regular C_{18} -packing might be too hydrophobic for these analytes. Furthermore, advances in LC-packings have led to the development of ultra HPLC (UHPLC) stationary phases. Likewise, a more recent study reported the use of UHPLC [35]. Even though it was not mentioned in the cited literature, the advantage of using UHPLC over HPLC is that it can be used for two-Dimensional LC (2D-LC) to separate and detect photodegradation species. Several publications have demonstrated that multidimensional liquid separation techniques yield a more comprehensive separation and detection of complex mixtures, such as food samples [88,89].

Flavonoids

The most commonly used separation technique for separation of

degradation products of flavonoids is HPLC. The use of TLC has also been reported in one study [54], but in modern days the use of HPLC is more convenient. Again, RPLC was the mode of choice when analysing flavonoids. C_{18} -columns have been used for analysing the photo-oxidation products of anthocyanidins [64], but C_{18} was the more common packing for the analysis of a large variety of photodegradation products [45,63]. Furthermore, a polymeric ODS-column can be used as well [55], for instance when mobile phases of very low pH are being used. As expected, a more recent study reported the use of UHPLC over HPLC, using a High Strength Silica (HSS) column [55]. This column is suited for UHPLC-analysis as it is resistant to very high pressures [90]. Very different is the separation technique that Gérard et al. used, which was cyclic voltammetry [73]. In cyclic voltammetry, electrochemical reactions such as redox reactions and anti-oxidising reactions can be monitored [91]. Since flavonoids can photo-oxidise into radical species, cyclic voltammetry is a very useful separation technique. As a suggestion, this technique could be useful besides regular HPLC-separation when the activity of anti-oxidants has to be determined.

Lipids

For lipid analysis, again, RPLC is the common separation method, with C_{18} as a stationary phase [65,76]. ODS-columns have been used for the analysis of fatty acids, the photodegradation products that are being formed after H-abstraction of lipids [65]. Furthermore, GC has been used as well [66], which is very useful when, for instance, the volatile photodegradation species have to be analysed.

Detection

When choosing an appropriate detection technique, the compatibility with the separation method should be considered. An overview of the detection techniques used in the cited literature for photodegradation studies in foods is also given in table 2.

Conventional detection methods

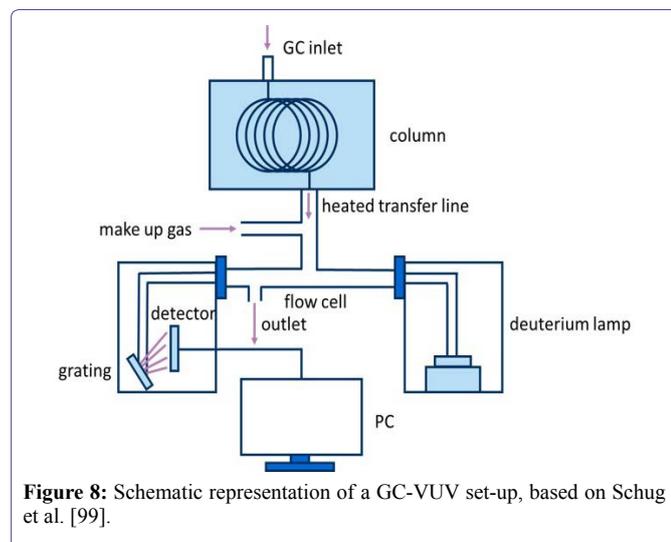
UV is by far the most common detection technique for the analysis of photodegradation products in foods and can be used for the characterisation of most of the photodegradation products present in food. An UV-detector is cheap and easy to operate and compatible with all conventional HPLC separation techniques. More sophisticated spectrophotometers, such as the Diode Array Detector (DAD) are also very commonly used detectors. However, since not all degradation products are UV- or Vis-active, alternative detection techniques have been used as well, such as a Mass Spectrometer (MS). MS analysis can be performed with different types of analysers. An older study reported detection with a mass sector analyser [82] and a single ion trap was also used in a more recent study [35]. Nevertheless, the most commonly used type of mass analyser is the quadrupole MS. Besides using a single analyser, a combination of multiple analysers, including quadrupole ion trap, has also been used in analysing the photodegradation products [33,65] and to gain an even better quantification power for more selective detection. While MS detection techniques are much more expensive than UV-detection they provide much more selectivity than UV detection and create the possibility of mass-based identification of compounds. A powerful type of mass spectroscopic detection is High-Resolution Mass Spectrometry (HRMS), in which analysers as Time Of Flight (TOF) and orbitrap are being used [92]. HRMS was applied by Fracassetti et al. for the analysis of

photodegradation products from flavonoids [55]. A TOF-MS has a broad mass range and has the advantage of having a high mass resolution making it especially suitable for the identification of unknown photodegradation products. However, the sensitivity of LC-HRMS is generally lower than that of LC with tandem quadrupole MS instruments. On the other hand, not only qualitative but also quantitative analysis can be performed with HRMS [93]. In particular, tandem MS with HRMS is a very powerful tool in the identification of photodegradation products in complex samples such as food [94].

Alternative detection methods

While UV and MS are the most commonly used detection techniques in combination with HPLC, other detection methods can be used as well for the analysis of photodegradation products that do not necessarily need to be combined with HPLC. For instance, Fracassetti et al. used both fluorescence detection and MS-detection for accurate characterisation of the degradation products [55]. This suggests that these alternative detection methods were used as an extra identification tool, rather than a powerful technique on its own. One of the alternative detection techniques used in the cited literature is Nuclear Magnetic Resonance (NMR) [82]. Even though NMR is non-destructive and has great identification power, its sensitivity is low whereas the cost of the instrument is much higher than that of a MS [95]. A very recent study by Gérard et al. applied another resonance-based technique: Electron Spin Resonance (ESR), in which radical activity can be measured [73,96]. Since many photo-induced degradation reactions lead to the formation of radicals, this ESR-detection, instead of NMR-detection, is a very useful technique for understanding the photodegradation reactions of food components. Various recent studies have already demonstrated the value of ESR-detection in food applications [97,98]. This means that ESR could be used as an alternative to MS-detection to monitor and gain a better understanding about the photodegradation mechanisms of food components. Other spectroscopic techniques that have been used for photodegradation analysis, include infrared [33] and fluorescence detection [55]. Both detectors are non-universal and LC-based and are thus only suitable for specific applications. Finally, a colourimeter has been used for the analysis of photodegradation products [73]. A colourimeter is a simple spectroscopic instrument that can measure the colour of a certain compound. It can be used to measure colour differences, hence the influence of light on the appearance of food components, as being performed by Chen et al. in 2019 [71]. Therefore, it gives straightforward information on the colour changing or colour loss of a food component.

A very upcoming detector in GC analysis is the Vacuum Ultraviolet (VUV) detector, which is in fact the GC equivalent of a regular UV detector (Figure 8). In contrast to a regular UV detector, the VUV detector is suited for volatile compounds. The most attractive feature of this detector is that it measures in the vacuum ultraviolet region, a region in which almost every compound shows absorbance [99]. Moreover, this detector can distinguish isomers and it can provide both qualitative and quantitative information [100,101]. The biggest drawback of this detector is that it is GC based and therefore not compatible with conventional HPLC. However, VUV could be a good detector for the analysis of volatile degradation products from lipid photodegradation.



From the literature we conclude that UV is the most common and easy detection technique which is compatible with conventional HPLC. For a detailed characterisation and quantification of photodegradation products, MS-detection or preferable tandem MS/MS detection is required, while for a comprehensive analysis of the photodegradation products HRMS is the best option. Besides these conventional detectors, also detectors recently developed were considered as promising. The VUV-detector is suggested as a promising detector for volatile components as it provides both quantitative and qualitative information. ESR could function as a useful tool for understanding the photodegradation mechanisms by monitoring the formation of radical species.

Concluding remarks

This review focused on the photodegradation of a selection of food components, i.e. carotenoids, chlorophylls, flavonoids and lipids, as well as on the analysis of the photodegradation products. Photochemical reactions of these compounds can occur directly or can be facilitated by a photosensitizer resulting in photo-oxidation, -isomerisation, H-abstraction, H-transfer and photolysis as the main photodegradation pathways. An overview was presented of the photodegradation reactions and the corresponding degradation products per compound class. Furthermore, a critical review of instrumental techniques to analyse photodegradation products in the best possible way was given. At first, a proper sample preparation should be executed to accurately extract the analyte from the complex food matrix. For the analyte separation, HPLC and UHPLC were the most commonly-used techniques, with GC being a suitable alternative for specific applications. UV- and MS-detection have shown to be the most conventional detection method while MS/MS and HRMS are powerful detection method for characterising the degradation products. Unconventional detectors are suggested to be used for specific applications. For instance, VUV-detection can be used for quantification and characterisation of volatiles and ESR for monitoring radical reactions. The analysis of photodegradation products from food is a challenging task and more extensive research is needed for a more comprehensive understanding of how food degrades and how to analyse the degradation species. In addition, it must be noted that large amount of photodegradation studies have been performed on

standards only and not on real food samples. Furthermore, this study only focussed on the photodegradation by natural light sources. Therefore, the influence of new artificial light sources, such as LED-lamps used in supermarkets, should be investigated in future studies as well.

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