Insight on the fundamentals of advanced oxidation processes. Role and review of the determination methods of reactive oxygen species

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Abstract

Advanced oxidation processes (AOPs) have known increased application to treat wastewaters containing recalcitrant compounds that are hardly degraded by conventional technologies. AOPs are characterized by the formation of strong oxidants such as hydroxyl radicals, superoxide anions, hydroperoxyl radicals and singlet oxygen, which react with the contaminant, contributing to its degradation. This paper provides an overview of the determination methods of reactive oxygen species, ROS, in the application of AOPs; the methods developed in the available literature for the detection and quantification of ROS are reviewed as a first step in the assessment and detailed description of the mechanisms involved in the oxidation reactions, focusing on the critical analysis of the main strengths and weaknesses presented by the probe molecules employed in the evaluated studies.

Keywords

Advanced oxidation processes, reactive oxygen species, hydroxyl radical, superoxide radical, hydroperoxyl radical, singlet oxygen

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Nomenclature

AAPD: anthryl-appended porphyrin dyad

AOPs: advanced oxidation processes

BA: benzoic acid

BHT: 2,6-di-tert-butyl-methylphenol

CA: chronoamperometry

CC: chlorocatechol

3-CCA: coumarin-3-carboxylic acid

CHD: 1,3-cyclohexanedione

CP: chlorophenols

CV: cyclic voltammetry

dHBA: dihydroxybenzoic acid

dHBA: dihydroxybenzoic acid

DMAX: 9-[2-(3-carboxy-9,10-dimethyl)anthryl]-6-hydroxy-3H-xanthen-3-one

DMPO: 5,5-Dimethyl-1-pyrroline N-oxide

DMSO: dimethyl sulfoxide

DNPH: 2,4-dinitrophenylhydrazine

DOC: dissolved organic carbon

DOM: dissolved organic matter

DPAN: 2,3-diaminophenazine

DPAX: 9-[2-(3-carboxy-9,10-diphenyl)anthryl]-6-hydroxy-3H-xanthen-3-one

DPCI: 1,5-Diphenylcarbohydrazide

DPCO: diphenylcarbazone

DTPA: diethylene triamine pentaacetic acid

ECD: electrochemical detector

EDTA: Ethylenediaminetetraacetic acid

EP: endoperoxide

ESR/EPR: electron spin/paramagnetic resonance

FC: ferrocytochrome C

FDMPO: 4-hydroxy-5,5,dimethyl-2-trifluoromethylpyrroline-1-oxide

FFA: furfuryl alcohol

FIA: flow injection analysis

GC-MS: gas chromatography – mass spectrometry

HBA: hydroxybenzoic acid

7HC: 7-hydroxycoumarin

HCHO-DNPH: formaldehyde-2,4-dinitrophenylhydrazine

HNPG: hydroxy- N,N’-(5-nitro-1,3-phenylene)bisglutaramide

$HO_2^{\bullet}$: hydroperoxyl radical

HPLC: high performance liquid chromatography

IBG: indoxyl-β- glucuronide

LC/ESI-MS/MS: liquid chromatography with positive ion electrospray ionization using a tandem mass spectrometer

LC-MS: liquid chromatography – mass spectrometry

MCLA: methoxy cypiridina luciferin analog

MTTA-Eu^{3+}: [4’-(10-methyl-9-anthryl)-2,2’:6’,2’’-terpyridine-6,6’’-diyl]bis(methylenenitrilo)tetrakis(acetate)-Eu^{3+}

NaTA: sodium terephthalate

NBD-Cl: 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole

NBT: nitroblue tetrazolium salt

Nitrone 4: 2-(2-pyridyl)-3H-indol-3-one-N-oxide

NHE: normal hydrogen electrode

NN: nitroxide-linked naphthalene

NPG: N,N’-(5-nitro-1,3-phenylene)bisglutaramide

$^1O_2$: singlet oxygen

$O_2^{\bullet -}$: superoxide radical

•OH: hydroxyl radical

7OH-3CCA: 7-hydroxycoumarin-3-carboxylic acid

5/6-OH-Phth: 5/6-hydroxy-2,3-dihydro-1,4-phthalazinedione

OHTA: hydroxyterephthalic acid

o-MHA: o-methylhydroxylamine

OPDA: o-phenylene diamine

PATA-Tb^{3+}: N,N,N’,N’-[2,6-bis(3′-aminomethyl-1′-pyrazolyl)-4-(9″-anthryl)pyridine] tetrakis (acetate)–Tb^{3+}

pCBA: p-chlorobenzoic acid

PDA: photo-diode array detector

Phth: phthalic hydrazide

PMT: photomultiplier tube

Rh-B: [9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride

RNO: N,N-dimethyl-4-nitrosoaniline

ROS: reactive oxygen species

$Ru(bpy)_3^{2+}$: tris(2,2'-bipiridin)rutenio (III)

SA: salicylic acid

SOSG: Singlet Oxygen Sensor Green reagent

SOTS: superoxide thermal sources

SVE: spiroadamantylidene- and aryloxy-substituted vinyl ether

TA: terephthalic acid

TTF: 4,5-dimethylthio-4’-[2-(9-anthryloxy)ethylthio]tetrathiafulvalene

TTFA: tetrathiafulvalene-anthracene dyad

XTT: 2,3-bis(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-carboxanilide

INTRODUCTION

The concern about the growth of surface and underground water contamination has increased over the years at the same time that the quality requirements of treated water are more demanding.[1-3] Advanced oxidation processes (AOPs) postulate as viable technologies for environmental remediation of wastewaters containing recalcitrant compounds, which cannot be easily destroyed by conventional treatments, through the generation of reactive oxygen species (ROS).[4,5] ROS comprehend not only free radicals, such as hydroxyl radical (•OH), superoxide radical ($O_2^{-\bullet}$) and hydroperoxyl radical ($HO_2^{\bullet}$), but also non-radicals such as singlet oxygen ($^1O_2$) and hydrogen peroxide (H_2O_2).[1] It has been proved that these species participate in the mineralization of organic compounds due to their non-selective and rapid reaction rates, being •OH the ROS with the highest reactivity.[6] Although a review of AOPs applications is beyond the scope of this manuscript, they have been successfully applied to the treatment of recalcitrant compounds present in actual wastewaters[7] from chemical industry (including fine chemical, pulp and paper, petrochemical, and pharmaceutical industry);[8-10] textile and tannery industry;[11] food and agro-industry;[12,13] drinking water, landfill leachate and urban wastewater;[14-18] and emerging pollutants.[19-22] So that insight in the mechanisms responsible for the oxidation reactions could greatly enhance the understanding and applicability of these processes.

Indirect methods based on the use of probes or scavengers have been developed and applied to selectively detect ROS generated in AOPs,[23-25] since their direct determination is only feasible on the sub-millisecond timescale owing to their short lifetime (10^{-10} s for •OH)[26,27]. These methods comprise the obtaining of a compound that reacts selectively, sensitively and unambiguously with the ROS under study[28,29] and, then, the quantification of either the loss of a reagent or the accumulation of a product. Some important aspects to consider when selecting an analytical method to determine ROS include: (i) sensitivity, (ii) selectivity and specificity towards the analyte of interest, (iii) measurements with sufficient fast time resolution, and (iv) stability of the probe and its reaction products. Other considerations that must be taken into account are related to the availability, robustness and cost of instrumentation and probe molecules.[28,30,31] Moreover, the choice of operating conditions is essential to avoid the reaction of ROS with themselves or prevent further reaction of the product.[32]

The indirect methods applied in the determination of ROS can be summarized in the following categories: (i) absorbance (UV/vis) probing methods, based on either the absorbance loss of the probe or the increasing absorbance of the product; (ii) fluorescence probing methods, where the reaction between the probe and the ROS leads to the formation of products showing strong fluorescence when they are excited at a specific wavelength; (iii) chemiluminescence probing methods, based on the reaction of a chemiluminogenic probe with ROS to yield a chemiluminescent product that irradiates light without being externally excited; (iv) spin-trapping methods, where the spin-trap agent reacts with the unpaired electron of the free radical; (v) electrochemical analysis based on cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical detection (ED).[28,33-35]

There are some papers gathering information about the main probes used with the aim to qualitatively/quantitatively determine the presence of ROS. Bartsoz[30] discussed the properties of the spectroscopic probes most commonly used for ROS detection in cellular systems, highlighting their limitations. Among spectroscopic techniques, the use of fluorescence methodologies to detect ROS generated in biological and physiological media have been reviewed by Gomes et al.[31] and Soh.[36] On the other hand, Lu et al.[37] evaluated the current state and the limitations of different chemiluminescence systems used in the identification of ROS in biological systems, pointing the necessity of future research to find specific chemiluminescent probes for ROS quantification.

It can be noticed that the above mentioned works are focused on the analysis of ROS mainly in biological media which is quite different from environmental aquatic media. In this sense, more recently, Burns et al.[28] collected a large number of references related with the use of probe molecules to qualify and quantify the ROS generated in sunlit waters characterized by the presence of dissolved organic matter (DOM) that acts as ROS scavenger. Nevertheless, the studies included in the cited review deal with the ROS naturally present or environmentally produced in fresh, marine and atmospheric waters and groundwaters, whereas to the best of our knowledge, a revision article covering the determination of ROS in AOPs has not been considered to date. A detailed study of ROS generation during the application of AOPs through their quantitative determination will allow the understanding and interpretation of the mechanisms involved along the advanced oxidation treatment of target compounds present in wastewaters. On this way, the aim of this work is to review the methodologies that have been applied for qualitatively/quantitatively determining the ROS produced by AOPs, taking into account the influence of the AOPs applied, the accuracy degree, the experimental conditions and the solution under study, and highlighting the main strengths and weaknesses of the different probes used.

In order to be concise in the presentation of the information gathered from literature, the AOPs have been grouped into the following categories: (i) Fenton processes that include conventional Fenton, Fenton-like and photo-Fenton; (ii) photolytic and photocatalytic systems; (iii) electrochemical technologies that take into consideration electro-oxidation, photoelectro-oxidation and photoelectrocatalytic processes, and electrical discharges; (iv) technologies based on ultrasounds such as sonolysis and sonocatalysis, and hydrodynamic cavitation; (v) γ-radiolysis and heavy ions.

With the aim to facilitate the comprehension of the potential of each probe used along the qualitative/quantitative determination of the ROS, a division into sections depending on the ROS analyzed has been made. Each section contains a table (Tables 1-3) with the following information: compounds used as probe together with the concentration range employed; AOPs in which the probe has been employed for ROS determination; the analytical features that include the analytical techniques used for ROS determination with specification of the measured product, analysis pH if a specific value is required and the concentration of ROS when quantitative values were provided; and finally, the analysis of the strengths and weaknesses of reported methods, which also includes the influence study of interferences.

DETERMINATION OF REACTIVE OXYGEN SPECIES INVOLVED IN ADVANCED OXIDATION PROCESSES

ROS are relatively short-lived molecules that contain oxygen atoms.[28,33-35] The radical ROS ($O_2^{\bullet-}$, $HO_2^{\bullet}$ and •OH) differ from the molecules (H_2O_2 and $^1O_2$) in the unpaired electrons that confer them higher reactivity. Regardless of the nature of ROS, it is essential to take into account the importance of the operating variables for their quantification. Among them, the probe concentration is of vital importance because a high concentration facilitates the complete trapping of ROS, minimizing side reactions with other organic compounds or radicals present in the solution that may result in an underestimation of the generated ROS.[37] This review is sectioned by ROS, being the studied species •OH, $O_2^{\bullet-}$/$HO_2^{\bullet}$ and $^1O_2$.

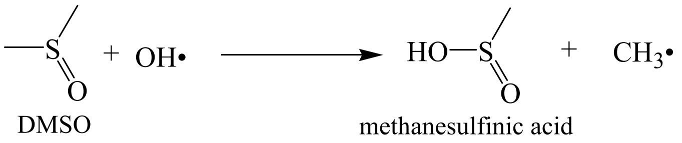
Hydroxyl radical

•OH is the most reactive oxygen radical with a very high standard potential, E°(•OH,H^+/H_2O), of 2.18 V vs. the normal hydrogen electrode (NHE) at pH 7.[28,37,38] •OH plays an important role in the degradation of organic compounds in natural waters owing to its high and non-specific reactivity, with second-order rate constants in the range 10^7-10^{10} $M^{-1}s^{-1}$.[4,32] Next, an overview of the main methods applied for the detection of •OH formed in AOPs of aqueous systems are detailed.

Absorbance probing methods

Absorbance probing methods are the most commonly used in the assessment of •OH generation, and consist of tracking either the loss of probe absorbance or the increase of the product absorbance. The equipment used in the works studied is a high performance liquid chromatograph (HPLC) or a spectrophotometer, both coupled with a UV/vis or photodiode array (PDA) detector.

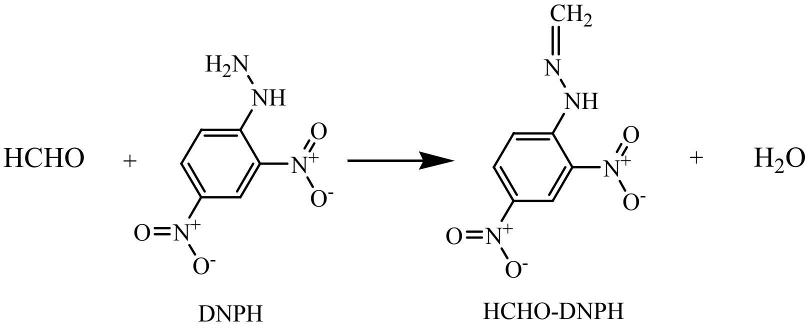
One of the probes most successfully applied to determine •OH is dimethyl sulfoxide (DMSO).[39-47] The reaction between DMSO and •OH starts a set of chain reactions leading finally to formaldehyde (reactions (1)-(3)).[39-45] Then, a derivatization procedure with 2,4-dinitrophenylhydrazine (DNPH) is carried out according to the EPA method 8315 A[48] to produce the corresponding adduct formaldehyde-2,4-dinitrophenylhydrazine (HCHO-DNPH, reaction (4)), which is finally analyzed by HPLC coupled with a UV detector (Table 1).



(1)

$$CH_3\bullet + OH\bullet \longrightarrow CH_3OO\bullet \quad (2)$$

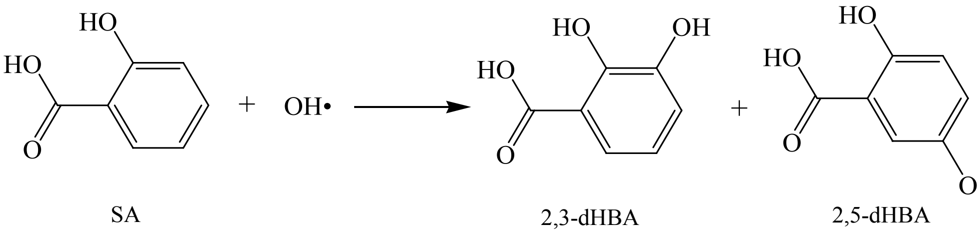
$$CH_3OO\bullet \longrightarrow HCHO + CH_3OH + O_2 \quad (3)$$



(4)

This procedure has been successfully applied in some AOPs such as three electrodes column,[39] photo-Fenton and photo-catalysis,[40,49] gas-phase dielectric barrier discharge,[41] high voltage electrical discharges studies[42] and Fenton,[43] allowing the study of the amount of •OH generated and the kinetic parameters under various operation conditions. However, other works where photo-Fenton,[40] photoelectro-Fenton and photolytic processes[44] were applied, showed underestimation of •OH generated due to the degradation of formaldehyde, which is the quantified product. On the other hand, faster oxidation processes such as electrochemical oxidation imply greater difficulty in the quantification of •OH because of the rapid generation, the non-selectivity and the high concentration of •OH in the proximity of the anode.[50] But, in general, this molecular probe provides better features over other probes, e.g., commercial availability and the advantage of leading to only one quantitative product (Table 1), as it will be shown through the document. Besides, the reproducibility of the results obtained has been endorsed by the alternative method based on sodium terephthalate (NaTA) where the observed differences between both methodologies are related to the employment of lower concentration of NaTA due to its minor solubility.[42] The main drawback is related with the derivatization reaction needed to quantitatively assess the generation of •OH.

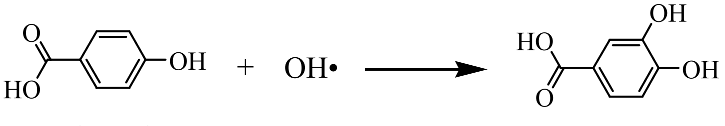
Alternatively, salicylic acid (SA) is an aromatic probe widely used for the determination of •OH. Basically, the quantification method is based on the hydroxylation reaction of SA (reaction (5)) to yield 2,3-dihydroxybenzoic acid (2,3-dHBA) and 2,5-dihydroxybenzoic acid (2,5-dHBA).



(5)

Although the quantification of the products concentration has been performed either with absorbance, fluorescence and electrochemical detectors, the measurements based on absorbance are the most frequently used. The quantification of •OH with this method has been successfully achieved in Fenton systems;[51,52] electrochemical methods such as pulsed plasma power[53] and electrochemical oxidation;[54] processes based on ultrasounds with or without photocatalysts[24,55-57] and hydrodynamic cavitation.[58,59] Most of them performed studies about the optimization of the operating conditions and the influence of many variables such as electrode materials, sonolysis frequency, pH, the presence of other organic compounds in the solution, concentration of SA, etc. According to the data summarized in Table 1, the use of SA as molecular probe provides sensitivity, reproducibility and repeatability in the analysis of •OH. Despite these strengths, it is important to select the proper ratio between SA and the quantification products, 2,3-dHBA and 2,5-dHBA because they have similar hydroxylation kinetic constants that can result in the underestimation of •OH. Another limitation that may interfere in this analysis is the formation of other reaction products than the quantification ones. Furthermore, it must be considered that the degradation of SA has been observed under certain operating conditions in electrochemical oxidation,[38,60,61] Fenton processes[62,63] or photolysis and photocatalysis systems,[62,64] fact that limits its application as molecular probe.

Benzoic acid and related compounds also belong to that group composed by aromatic compounds whose reaction with •OH is followed, mainly, by means of absorbance measurements. One of these related compounds refers to 4-hydroxybenzoic acid (4-HBA) which leads to 3,4-dihydroxybenzoic acid (3,4-dHBA, reaction (6)) after the hydroxylation reaction. It has been used as quantitative probe in Fenton,[26,27] photocatalytic and electrocatalytic processes.[23,65] An additional related compound applied to quantify the concentration of •OH refers to p-chlorobenzoic (pCBA). This probe, which has been evaluated in sonolytic[66,67] and photocatalytic systems,[5,68-70] leads to 4-chlorophenol (4-CP, reaction (7)) after its reaction with •OH. Alternatively, benzoic acid (BA), whose hydroxylation reaction leads to the formation of the corresponding isomers of HBA (reaction (8)),[2,4,71-76] was employed as probe to calculate the concentration of the photogenerated •OH in natural waters[71] and those produced in Fenton and photolysis processes.[2,73-75] The results dealing with the determination of •OH using BA[71] and pCBA[70] were validated using methanol (reactions (9) and (4)) and n-propanol[73] (reactions (10) and (11)) as molecular probes. Nevertheless, as it has been mentioned for SA, an important limitation is related with further reaction of the quantitative product as it was observed under specific experimental conditions for 4-HBA in Fenton process,[27] pCBA in photocatalysis[5] and sonocatalysis,[5,69] and BA in a Fenton-like process (Table 1).[76]



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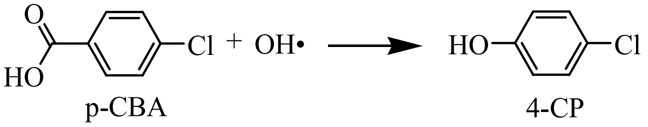
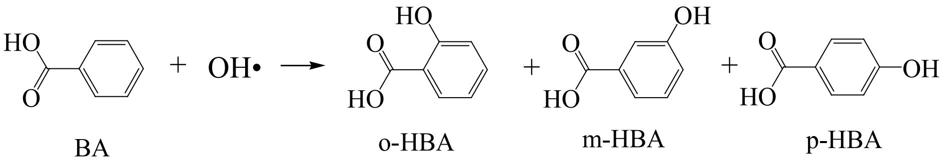
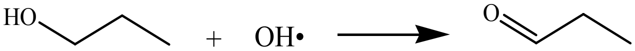


(7)



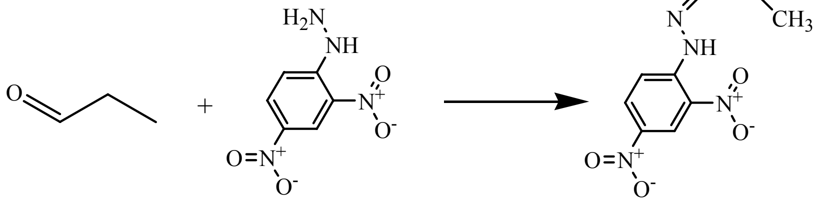
(8)

$$CH_3OH + OH\bullet \longrightarrow HCOOH + H_2O \qquad (9)$$



propanol propionaldehyde

(10)

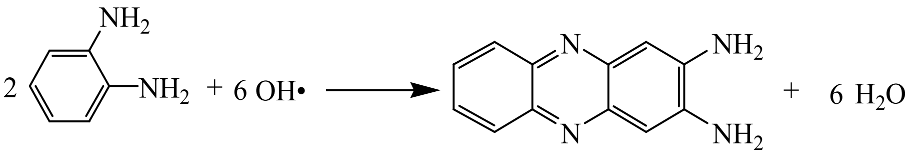


propionaldehyde DNPH propionaldehyde-DNPH

(11)

Benzene has been also used as •OH trapping in Fenton and photocatalytic processes allowing the measurement of •OH concentration through the formation of phenol (reaction (12)) in different systems such as Fe(III)-citrate,[77] Fe(III)-piruvate,[78] river water, NO_3^-, NO_2^- and H_2O_2,[79] and aqueous suspension of montmorillonite (mineral clay).[80] Nevertheless, when powerful AOPs were applied, as is the case of electrochemical oxidation, the mineralization of either the probe and its quantitative product was observed.[81] A related compound, the substituted benzene o-phenylendiamine (OPDA), was used by Fang et al.[82] as probe for quantitatively identifying the amount of •OH generated in photo-Fenton through the quantification of the reaction product 2,3-diaminophenazine (DAPN) (reaction (13)). This probe displayed a good selectivity towards •OH with a simple analytical method.

(12)



OPDA DAPN

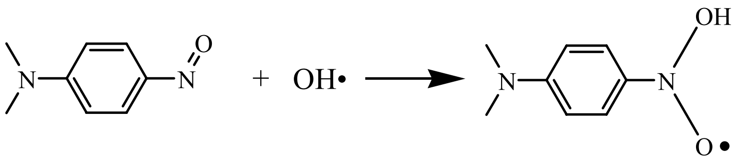
(13)

One more molecular probe applied to determine the kinetic rate constant of •OH generation during radiolysis of natural waters is SCN^-, through competitive kinetics with DOM (reactions (14) and (15)).[83]

$$OH\bullet + DOM \longrightarrow H_2O + DOM\bullet \qquad (14)$$

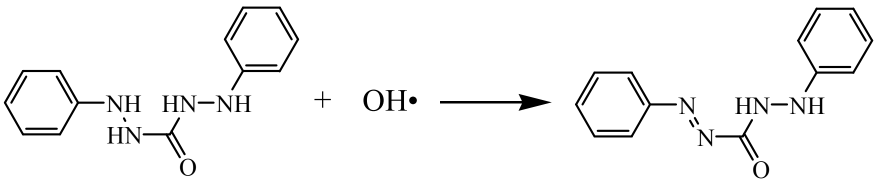
$$OH\bullet + 2\ SCN^{-} \longrightarrow OH^{-} + (SCN)_2^{-\bullet} \qquad (15)$$

On the other hand, there are some probes that have been used with the purpose of quantifying the formation of •OH but are not advisable because they are not selective in the assessment of •OH. On this sense, the use of 4-chlorophenol (4-CP) led to the generation of numerous products of quantification, in addition to 4chlorocatechol (4CC), which in turn were further oxidized in Fenton,[84] photolytic[85] or photoelectrocatalytic processes.[86] Another example is the use of quinoline, which led to the formation of numerous products until their complete mineralization in photo-Fenton and photocatalysis systems.[87,88] Moreover, compounds such as p-Nitrosodimethylaniline (RNO)[33,89-91] (reaction (16)) and 1,5-diphenyl carbazide[1,92] (DPCI, reaction (17)) react with other ROS pointing out the need to add scavengers to quantitatively measure the concentration of each ROS specie.



RNO RNO-OH

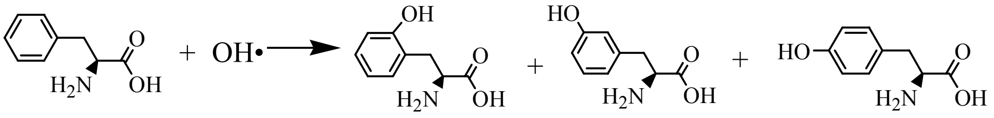
(16)



DPCI DPCO

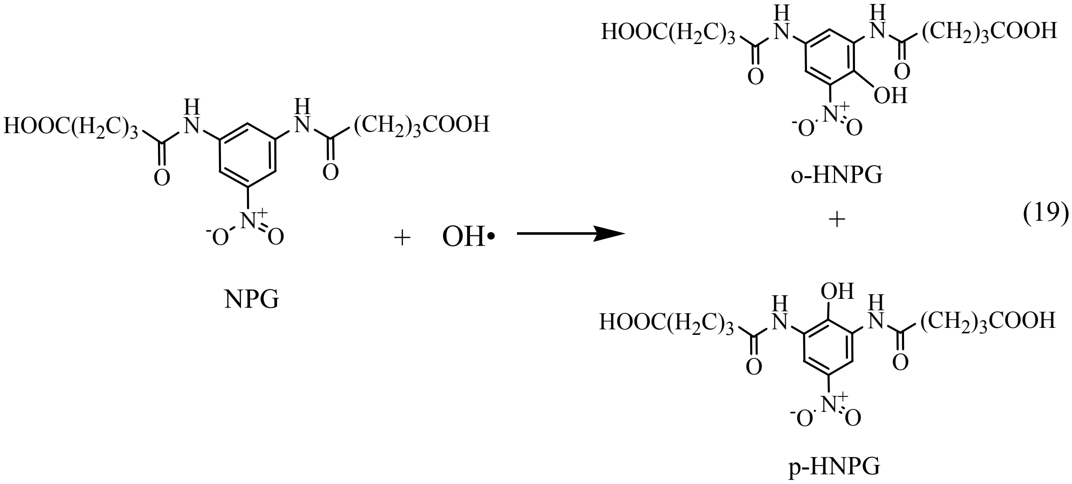
(17)

Though not directly related to the quantitative/qualitative •OH determination, some of these molecular probes mentioned above such as 4-HBA,[65] BA[4] or p-CBA,[70] and other new ones were employed in the assessment of the scavenging capacity of different antioxidants that can be present in aqueous and biological media, as it is the case of [9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride (Rhodamine B, RhB) that produces tyrosine isomers in the hydroxylation reaction[93,94] (reaction (18)) and N,N'-(5-nitro-1,3-phenylene)bisglutaramide (NPG) that leads to the ortho and para hydroxy isomers[95] (HNPG, reaction (19)).



phenylalanine o-tyrosine m-tyrosine p-tyrosine

(18)

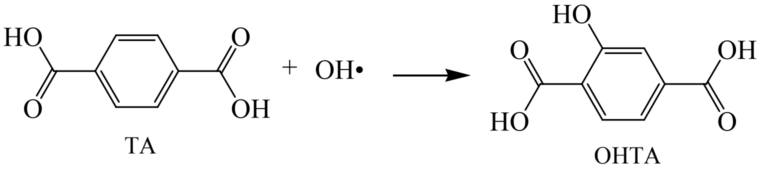


(19)

Fluorescence probing methods

The basis of a fluorescence probing method consists on the appearance of a fluorescence product after the reaction of the molecular probe with •OH. The excitation of the reaction product at a specified wavelength results in the emission of fluorescence which is then recorded and translated in terms of concentration through a calibration curve. The equipment employed was basically a HPLC or a spectrophotometer, both coupled with a fluorescence detector.

In this sense, compounds such as terephthalic acid (TA, (reaction (20))) and sodium terephthalate (NaTA),[25,29,42,96-102] coumarin (reaction (21)),[6,103-111] coumarin-3-carboxylic-acid (3CCA, reaction (22)),[112,113] and ninhydrin(reaction (23)),[114] have been successfully applied in the quantification of •OH generated when Fenton, photocatalysis, electrochemical technologies, ultrasounds, hydrodynamic cavitation, γ-radiolysis and heavy ions were applied. In some of these studies, the influence of operational conditions such as flow-system variables, pH, catalyst concentration, probe concentration, presence of other interferences, etc., were evaluated.[114] Moreover, coumarin and TA/NaTA have been also found to serve as adequate probes for the direct assessment and comparison of the scavenging potential of different antioxidant compounds.[65,115] Some of the main strengths displayed by these methods are simplicity, sensitivity, reproducibility and accuracy. However, some issues must be considered, as it is the case of fluorescence pH-dependence, formation of other hydroxylated products in addition to the quantifiable ones, and degradation of the quantification product under specific operating conditions.[116]



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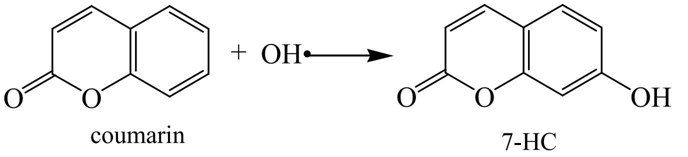
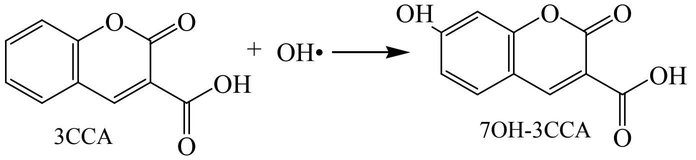


(21)



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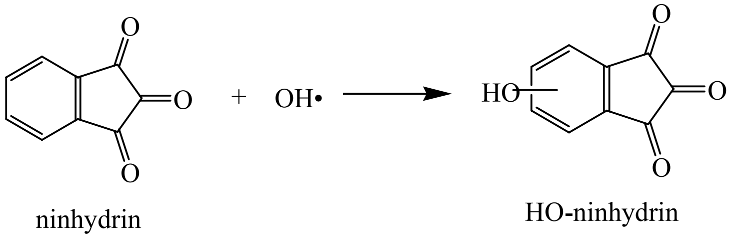
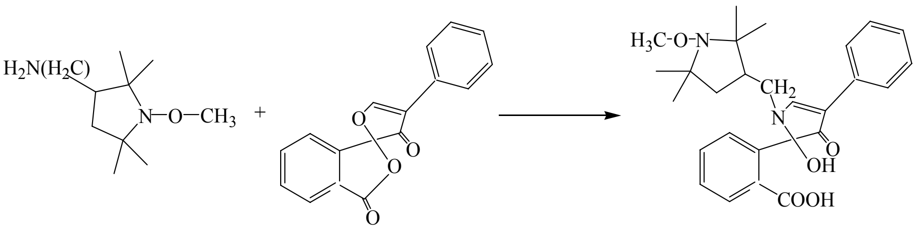


(23)

On the other hand, fluorescence measurements based on the products of SA hydroxylation were oriented towards the study of the influence of some parameters such as flow-rate and solution pH in the •OH concentration when hydrodynamic and ultrasonic cavitation were applied.[59] Finally, there are some works that employ DMSO as molecular probe to qualitatively study the generation of •OH in Fenton[45,46] and photochemical[47] systems. Here, the derivatization reactions differ from that used in absorbance methods and are based on (i) the reaction of formaldehyde, produced from the reaction between DMSO and •OH through reactions (1)-(3), with 1,3-cyclohexanedione (CHD) and ammonium according to reaction (24), where the fluorescence emitted by $C_{13}H_{15}O_2N$ was correlated to the concentration of formaldehyde,[45] and (ii) the addition of a nitroxide-linked naphthalene (NN) which reacts with the methyl radical formed according to reaction (1) to yield o-methylhydroxylamine (o-MHA)[46,47] and a fluorescent compound that is then analyzed (reactions (25) and (26)).[47] In spite of being sensitive and simple methods, fluorescence probing methods based on DMSO required heating during the derivatization process or the addition of an additional compound (NN) which has to be synthesized in the laboratory.

$$HCHO + CHD + NH_3 \longrightarrow C_{13}H_{15}O_2N \tag{24}$$

$$CH_3\bullet + NN \longrightarrow \text{o-MHA} \tag{25}$$

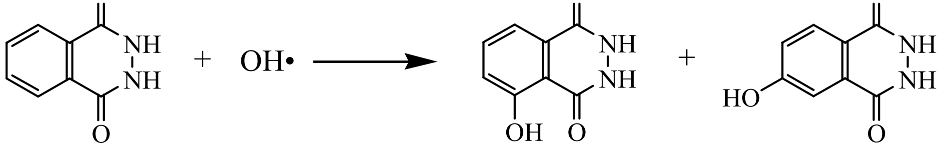


o-HMA fluorescamine fluorescent product

(26)

Chemiluminescence probing methods

In chemiluminescence probing methods, the reaction between a chemiluminogenic compound and •OH produces an excitation that is measured by a luminometer or a photomultiplier tube. Within this group, phthalhydrazide (Phth) has been postulated as feasible molecular probe due to its selective reaction with •OH leading to the production of 5- and 6-hydroxy-2,3-dihydro-1,4-phthalazinedione (5OH-Phth and 6OH-Phth, (reaction (27)), which are chemiluminescent compounds (Table 1).[117-119] The viability of using Phth as molecular probe for the quantification of •OH was studied by analyzing the oxidation pathway and the influence of some experimental parameters, such as pH and the presence of other compounds in the solution, in the generation of chemiluminescence when γ-radiolysis and Fenton-like technologies were applied. They observed that the chemiluminescence of hydroxylation products was pH-dependent and the luminescence emission of 6OH-Phth was 40 times lower than 5OH-Phth, which could result in an underestimation of •OH concentration.



Phth 5OH-Phth 6OH-Phth

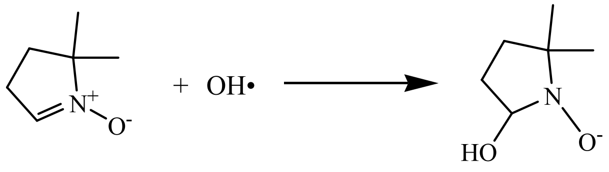
(27)

Two additional probes, tris(2,2'-biprridine)ruthenium (III) ($\mathrm{Ru(bpy)_3^{2+}}$, reaction (28))[120] and Indoxyl-β- glucuronide (IBG)[121] were used to qualitatively characterize the scavenging capacity of different antioxidants through the chemiluminescence produced in a Fenton process. Despite the fact that these molecular probes are selective towards •OH, they suffer of instability of the molecular probe and commercial unavailability, respectively.

$$\mathrm{Ru(bpy)_3^{3+} + OH\bullet \longrightarrow [Ru(bpy)_3^{2+}]^{*} + 0.5\ O_2 + H^{+} \longrightarrow Ru(bpy)_3^{2+} +}\ h\nu \qquad (28)$$

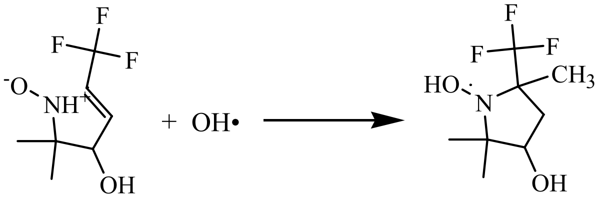
Spin-trapping methods

One of the oldest techniques in the determination of •OH is the spin-trapping method, which usually involves organic nitrone or nitroso compounds that after the reaction with •OH lead to nitroxide adducts, which are measured by electron spin/paramagnetic resonance spectroscopy (ESR/EPR). Compounds such as 5,5-dimethyl-1-pyrroline N-oxide (DMPO), 4-hydroxy-5,5,dimethyl-2-trifluoromethylpyrroline-1-oxide (FDMPO), 3-carboxyproxyl and 2-(2-pyridyl)-3H-indol-3-one-N-oxide (referred as nitrone) belong to this group. DMPO is, perhaps, the spin trap and one of the probes most used for the quantitative determination of the •OH generated in different AOPs. Although some works were focused on monitoring the DMPO-OH formation (reaction (28)) for example in photocatalysis,[122] sonolysis[66,67,123] and Fenton[124] systems, in general, most of them analyzed and compared the signals recorded during the EPR technique without quantifying the generated product when electrocatalysis,[125,126] Fenton[125-128] and photocatalysis[84] were applied. There are also examples in which the main objective is the calculation of kinetic constants of benzenes and halobenzenes by means of a competitive kinetic method with DMPO,[129] the scavenging percentage of different phenolic compounds[130] and the evaluation of different ROS generated in a photoelectrocatalytic system in aqueous and methanol media.[86] Although high sensitivity was observed using DMPO as molecular probe, its non-selectivity is an important drawback that has to be considered because DMPO may react with $\mathrm{O_2^{\bullet-}}$, $\mathrm{^1O_2}$ and ROO•.



(28)

Additionally, FDMPO, a variety of DMPO, was synthetized in the laboratory for the viability study of its use as spin-trapping agent in the detection of free radicals such as •OH (reaction (29)), $\bullet CH_3$ and $\bullet CH_2OH$ in a Fenton system,[131] although no quantitative results related to the concentration or generation rate of •OH were presented. FDMPO displayed higher stability than DMPO but it was also non-selective towards •OH. On the other hand, the spectroscopic measurement of proxyl-NOOH, produced from the reaction of 3-carboxyproxyl with •OH (reaction (30)), was carried out to quantify the •OH in a photocatalytic system.[132] Nevertheless, proxyl-NOOH was not the unique product and it can be generated after the reaction of conduction band electrons with 3-carboxyproxyl. Finally, nitrone (synthetized in the laboratory) was also employed as probe in the determination of •OH, although its efficiency to spin trap these radicals was limited (reaction (31)).[133]



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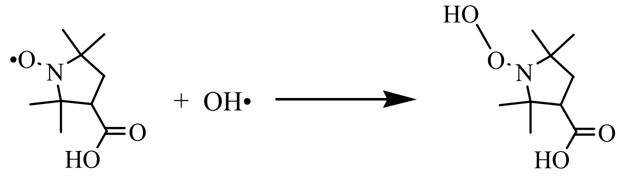

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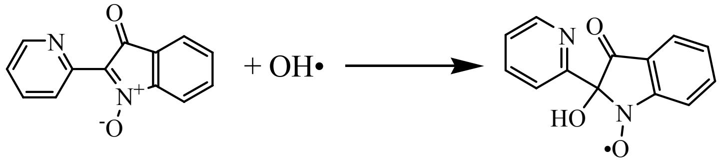


(31)

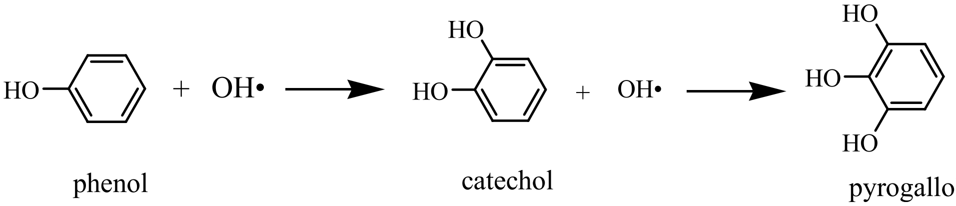
Electrochemical analyses

The electrochemical analyses gathered in this review are based on cyclic voltammetry (CV), chronoamperometry (CA), capillary electrophoresis and HPLC coupled with electrochemical detection (ED). Electrochemical analyses are focused on the correlation between the electrochemical signal recorded and the measure of the generated •OH obtained via other probing method. In this sense, Mahé et al.[134] correlated the amperometric signal recorded in cyclic voltammetry with the luminescence generated as consequence of the reaction between Phth and •OH. In a different work, Gualandi and Tonelli[24] used an electrode covered by a polyphenol film and the redox pair $Ru(NH_3)_6^{3+}/Ru(NH_3)_6^{2+}$. The relationship between the uncovered area (reaction (32)), as consequence of the reaction between the polyphenol film and the •OH produced in Fenton and photocatalysis processes, and the concentration of •OH was established through the chromatographic method using SA. Once this relationship was known, the •OH concentration could be determined estimating the extent of the polymeric film degradation, quantified by means of the electrochemical behavior (CV and CA) of the redox probe $Ru(NH_3)_6^{3+}$ (reaction (33)). Both electrochemical analyses require the previous development of another probing method which allows the establishment of a correlation between the electrochemical signal and the amount of •OH generated.

$$\text{polyphenol film} + \text{OH}\bullet \longrightarrow \text{electrode with uncovered area} \quad (32)$$

$$Ru(NH_3)_6^{3+} + e^- \longrightarrow Ru(NH_3)_6^{2+} \quad (33)$$

On the other hand, electrochemical measurements based on the products of SA hydroxylation were oriented towards the study of the viability and the optimum conditions to selectively separate the signals corresponding to the probe and the quantification products (2,3-dHBA and 2,5-dHBA).[135,136] Alternatively, phenol[137,138] and pyrocatechol (catechol)[137] have been used to quantify the concentration of •OH by electrochemical analyses in Fenton treatment. Nevertheless, after 5 minutes of Fenton process or when electrochemical oxidation was applied[138] the degradation of phenol and its oxidation intermediates were observed (reaction (34)) resulting in an underestimation of •OH concentration.



(34)

As a summary of the reviewed information regarding the analysis of •OH, some requisites, obviating the analytical equipment requirements, that must be taken into account in the selection of the adequate molecular probe include: (1) the selectivity of the selected probe where organic compounds such as benzoic acid and related compounds, 3-CCA, DMSO, phenol, SA and TA/NaTA displayed high selectivity towards •OH, whereas DMPO, nitrone and DPCI present the lowest selectivity; (2) the stability of the quantifiable compound, where DMPO and 3-carboxyproxyl or phenol present the lowest stability; (3) the commercial availability of the reagents and products, as is the case of DMSO, SA, benzoic acids, phenols and coumarin among others which have not been prepared in the laboratory such as FDMPO, IBG, quinoline and fluorescence methods based on DMSO; (4) the possible formation of several reaction products that makes the quantification tedious and less accurate, e.g., in the use of SA, benzoic acids, benzene, phenol, etc. where the formation of catechol and hydroquinone is usual; (5) those probes that produce various fluorescent species with different fluorescence intensity as is the case of Phth and 3-CCA; (6) the advanced oxidation process under study and experimental conditions. In this sense, absorbance probing method based on DMSO is one of the probes that better fit the aforementioned requests. On the other hand, NaTA and SA seem to fulfill the requirements to be an adequate probe in spite of having some weaknesses related to solubility and formation of several hydroxylation products, respectively.

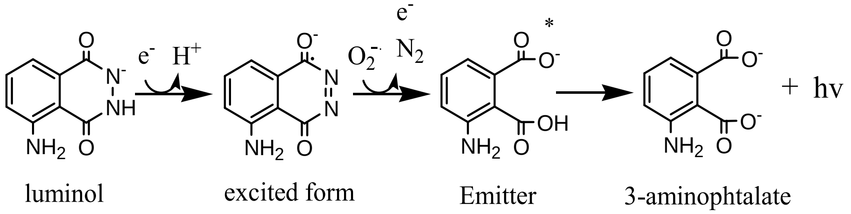
Superoxide and hydroperoxyl radical

$O_2^{-\bullet}$ is produced as a result of the donation of an electron to oxygen,[37] and its protonation leads to $HO_2^{\bullet}$, although in aqueous media $O_2^{-\bullet}$ predominates over $HO_2^{\bullet}$ [28,139] (reaction (35)). Though $O_2^{-\bullet}$ is relatively inactive by itself owing to resonance stabilization,[28] in aqueous media at neutral pH protons promote a rapid reaction leading to H_2O_2 (reaction (36)).[140] Its standard potential, E°($O_2^{-\bullet}$,H^+/H_2O_2) = 0.95 V vs. NHE at pH = 7 , is less than half of the corresponding to •OH. The second-order rate constants are not as high as in the case of •OH reaction, but they can reach the range 10^7-10^{10} $M^{-1}s^{-1}$ when $O_2^{-\bullet}$ reacts with luminol, superoxide dismutase (SOD), different quinones, etc.[139] Direct measurement of $O_2^{-\bullet}$ is complicated because there are several species, such as H_2O_2, that absorb light irradiation at the same wavelength.[139,141] The presence of complexing agents and salts in the solution, pH and type of solvents influence the half-life time of $O_2^{-\bullet}/HO_2^{\bullet}$.[141] The main advantages and limitations described by the authors of the analyzed literature are summarized in Table 2.

$$HO_2^{\bullet} \rightleftharpoons O_2^{-\bullet} + H^+ \qquad pK_a = 4.69 \qquad (35)$$

$$2\,O_2^{-\bullet} + 2\,H^+ \rightleftharpoons H_2O_2 + O_2 \qquad K_{pH\,7} = 4\cdot 10^{20} \qquad (36)$$

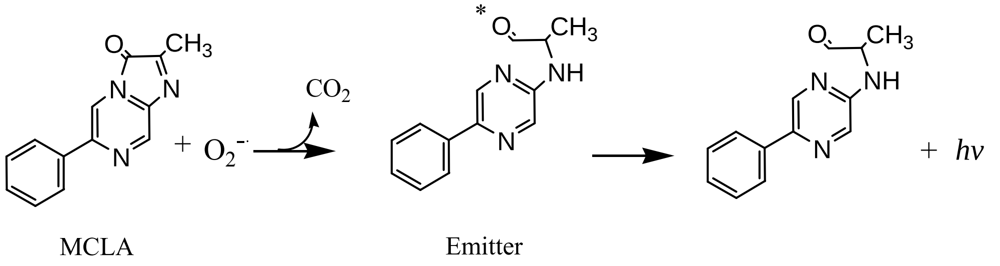
The most used probe for the quantitative determination of $O_2^{-\bullet}$ is luminol, leading to the generation of chemiluminescence (reaction (37)) that is then measured by a luminometer. This method has been applied to measure $O_2^{-\bullet}$ concentration in Fenton systems.[142] In addition, the concentration of $O_2^{-\bullet}$ has been successfully quantified in photocatalytic systems in which, furthermore, additional parameters were evaluated: study of the effect of crystalline structure in the generation of ROS;[100] variability of ROS production depending on the photocatalyst;[100,143,144] influence of H_2O_2 and inorganic species on the behavior of the $O_2^{-\bullet}$ produced;[101,145,146] monitoring and differentiation, with a time-resolved technique, of the luminescence generated by the reaction of luminol with $O_2^{-\bullet}$ or with H_2O_2;[145,147] and generation and deactivation study of $O_2^{-\bullet}$ on the TiO_2 surface.[145] Nevertheless, luminol presents important weaknesses as its non-selectivity towards $O_2^{-\bullet}$ and the background noise during the luminescence analyses which restrict its use to alkaline pH.



(37)

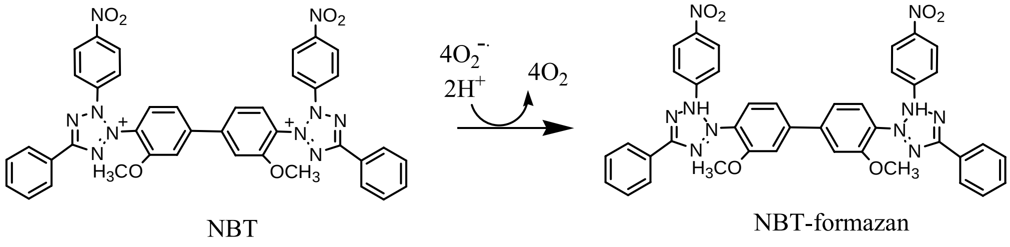
The methoxy cypiridina luciferin analog (MCLA) is another molecular probe used in the indirect determination of $O_2^{-\bullet}/HO_2^{\bullet}$ by a chemiluminescent method. The progress of the concentration of $O_2^{-\bullet}$

was successfully quantified through the measurement of the chemiluminescence generated (reaction (38)) after photocatalysis experiments with the aim of comparing the activity of silica-coated with uncoated TiO_2,[107] and the activity and reaction mechanisms of modified TiO_2 and WO_3.[143] Data of $O_2^{-\bullet}$ generated from superoxide thermal sources (SOTS) have been included also in Table 2. Heller and Croot[141] developed tools for the numeric analysis and the investigation of the origin sources of $O_2^{-\bullet}$, as well as the study of the adequate method for determining its concentration in marine waters. On the other hand, Mahé et al.,[134] similarly as they did when evaluating the presence of •OH, correlated the amperometric signal recorded in cyclic voltammetry with the luminescence generated as a consequence of the reaction between MCLA and $O_2^{-\bullet}$. The selectivity towards $O_2^{-\bullet}$ is enhanced by using MCLA with respect to luminol, but also reacts with $^1O_2$. On the other hand, MCLA can be used at different pH and not only in alkaline media.



(38)

A group of usable compounds as molecular probes includes tetrazolium salts. Among them, Nitroblue tetrazolium (NBT) and 2,3-Bis(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-carboxanilide (XTT) were used in photocatalytic systems to identify the generation of $O_2^{-\bullet}$ by absorbance measurements, throughout the decrease in the absorbance registered at the wavelength of 530 nm (reaction (39))[68,148,149] and 470nm (reaction (40)),[68,90] respectively. Both present good selectivity but water solubility problems may arise specially using NBT as molecular probe.



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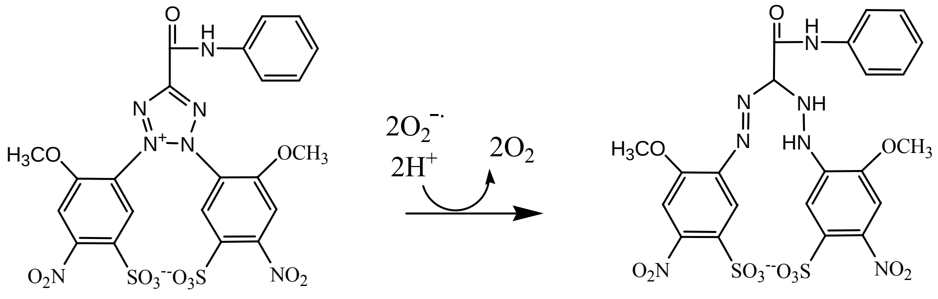


XTT XTT formazan

(40)

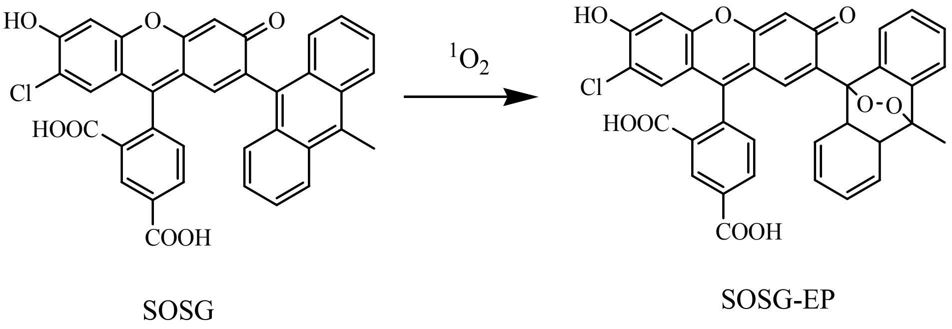
The main features of the use of ferrocytochrome C (FC) and 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl) as $O_2^{-\bullet}$ probe, which are presented in Table 2, was studied by Heller and Croot.[141] They observed a $O_2^{-\bullet}$ overestimation when NBD-Cl was used as molecular probe due to interfering reactions during the decomposition of SOTS-1. Nevertheless, the underestimation of $O_2^{-\bullet}$ concentration took place when FC was employed in presence of H_2O_2. Finally, the research group of Kwon developed a kinetic method to quantify $O_2^{-\bullet}/HO_2^{\bullet}$ in Fenton and photocatalytic systems based on the hydroxylation of NaTA[150] or BA,[150-152] identifying the half-life time of $O_2^{-\bullet}/HO_2^{\bullet}$, their concentration and the influence of pH. They saw that half-life is pH-dependent and its highest value corresponds to pH 9. On the other hand, a specific experimental setup based on a continuous flow injection was required for the determination of $O_2^{-\bullet}/HO_2^{\bullet}$ with NaTA and BA by using a kinetic method. BA displayed lower sensitivity than NaTA owing to the interference of by-products of BA which would lead to an error on the detection of $O_2^{-\bullet}/HO_2^{\bullet}$[150]

As concluding remarks, it is crucial to consider the importance of pH in the generation and reactivity of $O_2^{-\bullet}/HO_2^{\bullet}$ because of their higher stability in alkaline media as stated in several studies.[35,101,147] Among the different compounds tested as molecular probes in different AOPs, although luminol is the most applied one to determine $O_2^{-\bullet}$, MCLA, NBT and XTT may have easier application, simpler implementation and better results than luminol due to the fact that analytical quantification techniques are simpler and, above all, these probes are less affected by the presence of interferences such as H_2O_2, metals and ionic species that may oxidize the probes.

Singlet oxygen

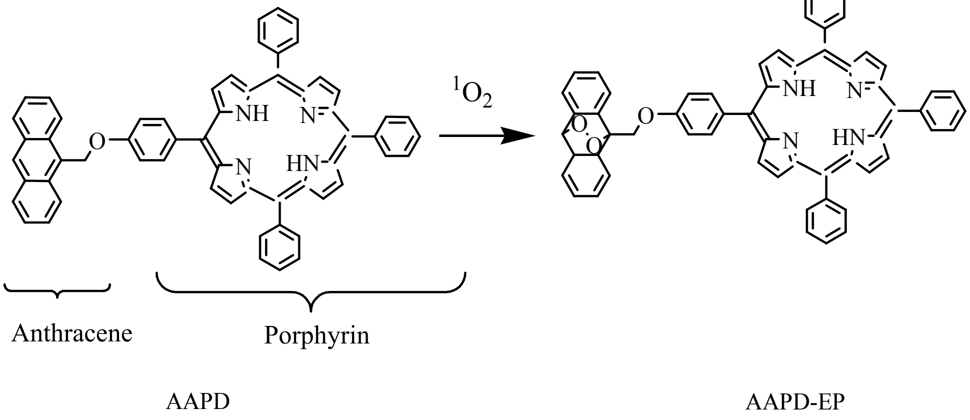
$^1O_2$, the lowest excited state of molecular oxygen, can be used as a highly active oxidant in chemical, biological and environmental systems.[37,153,154] $^1O_2$ can be easily generated in solution by energy transfer from excited photosensitizers or chemically, which are the most common procedures.[28,154-157] $^1O_2$ has a standard potential E°($^1O_2$/ $O_2^{-\bullet}$) equal to 0.65 V vs. NHE at pH 7 and its lifetime in aqueous solution depends on the presence of scavengers (DOM in natural waters), being 4 μs in pure water.[28,155] The direct measurement of the luminescence emitted by $^1O_2$ has been carried out at 1270 nm, althought sometimes the weak signal recorded hinders the application of this direct analytical method.[158,159] The research group of Daimon[160-162] studied the production of $^1O_2$ in TiO_2 photocatalysis, monitoring its phosphorescence and lifetime under various reaction conditions such as: presence of additives (KBr, KSCN, KI, H_2O_2), pH, size of TiO_2 particles and gaseous environment (N_2 or O_2), and also investigating the mechanism that leads to the formation of $^1O_2$. Nevertheless, indirect methods have been also developed with the aim of taking a step further towards improving its quantitave determination. Mainly, these indirect methods are based on the addition of a probe which after reacting with $^1O_2$ leads to the formation of a fluorescent or luminescent product. The main strengths and drawbacks of the use of the different probes are reported in Table 3.

One of the probes used in the determination of $^1O_2$ is the Singlet Oxygen Sensor Green reagent (SOSG) that reacts with $^1O_2$ leading to the formation of a highly fluorescent endoperoxide (SOSG-EP) (reaction (41)), which is then measured by spectrofluorometry. Its feasibility for the quantitative measurement of $^1O_2$ generation has been studied when Rose Bengal was used as photosensitizer in an air-saturated phosphate buffered.[163] Furthermore, the assessment of the dependence of the initial concentration of SOSG and photosensitizers on the fluorescence intensity was carried out. Another commercially available probe is furfuryl alcohol (FFA), which allowed the determination of $^1O_2$ concentration in photolytic and photocatalytic systems starting from different aqueous matrixes and assessing the pH influence.[68, 164] Furthermore, the presence of some ions such as Cl^- and N_3^- was also evaluated in these works with the aim of studying their influence in $^1O_2$ scavenging. The main advantage of using SOSG and FFA as molecular probes, together with their good selectivity, is the commercial availability of these compounds.



(41)

In contrast to SOSG or furfuryl alcohol, which are commercially available, most of the specific compounds used along the quantitative determination of $^1O_2$ have been synthesized in the laboratory. These compounds are based in relatively complex aromatic structure in which the reaction with $^1O_2$ yields a fluorescent/luminescent endoperoxide. One of these probes is anthryl-appended porphyrin dyad (AAPD), which behavior in the presence of other ROS was studied in a Fenton-like system (MoO_4^{2-}/H_2O_2).[165] The fluorescent product after the reaction with $^1O_2$ is shown in reaction (42). Alternatively, the research group of Nagano designed and synthesized 9-[2-(3-carboxy-9,10-diphenyl)anthryl]-6-hydroxy-3H-xanthen-3-one (DPAX)[166] and 9-[2-(3-carboxy-9,10-dimethyl)anthryl]-6-hydroxy-3H-xanthen-3-one (DMAX)[167] (reactions (43) and (44)), giving the reaction rates of DPAX and DMAX with $^1O_2$.



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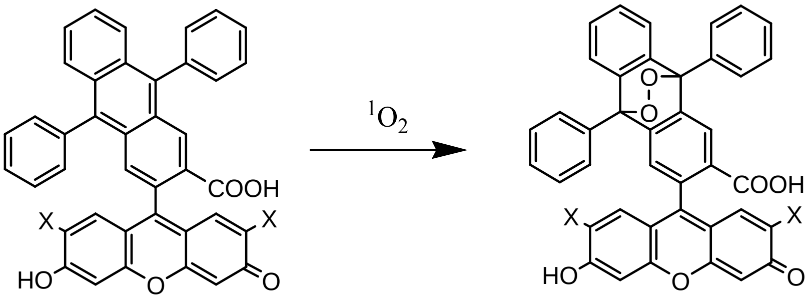
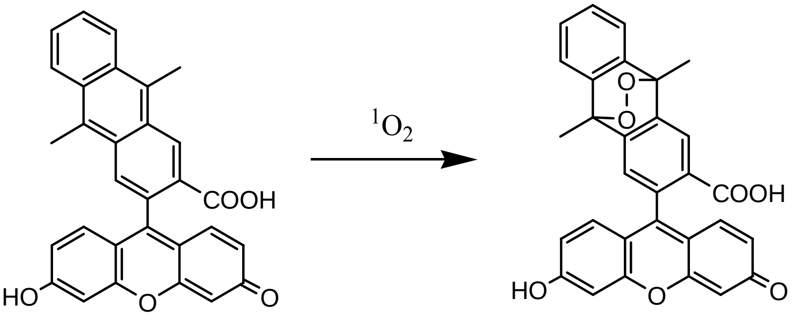
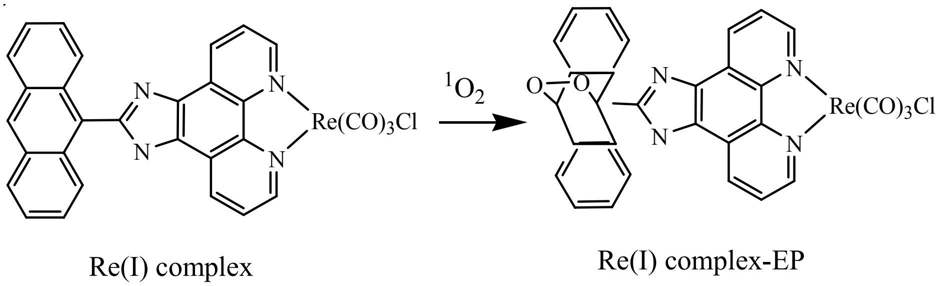


DPAX DPAX-EP (43)



DMAX DMAX-EP (44)

Another group that has also demonstrated high selectivity and good response towards $^1O_2$ comprises chelate-based luminescence probes. Rhenium complex, Re(CO)$_3$Cl(aeip) [aeip: 2-(anthracen-9-yl)-1-ethyl-imidazo[4,5-f][1,10]phenanthroline],[153] europium complex, 4’-(10-methyl-9-anthryl)-2,2’:6’,2’’-terpyridine-6,6’’-diyl]bis(methylenenitrilo)tetrakis(acetate)-Eu^{3+} (MTTA-Eu^{3+}),[168] and terbium complex, N,N,N’,N’-[2,6-bis(3′-aminomethyl-1′-pyrazolyl)-4-(9″-anthryl)pyridine] tetrakis (acetate)–Tb^{3+} (PATA-Tb^{3+}),[169] were also synthetized in laboratory and react with $^1O_2$ yielding luminescent endoperoxides (reactions (45)-(47)). The assessment of the influence of experimental parameters such as pH and the presence of other reactive species (•OH, H_2O_2, ONOO$^-$) on the luminescence intensity and lifetime of the generated endoperoxide was carried out (Table 3). Re(I) displayed some advantages over MTTA-Eu^{3+} and PATA-Tb^{3+}, such as its lower detection limit and the fact that Re(I) may be excited under visible light.



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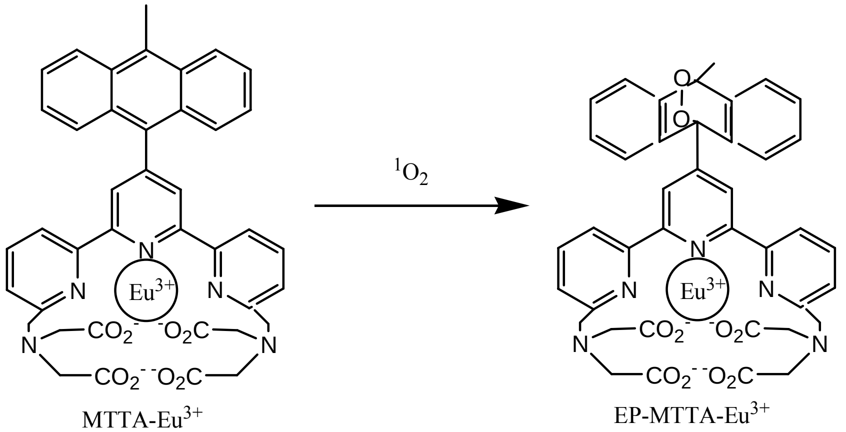
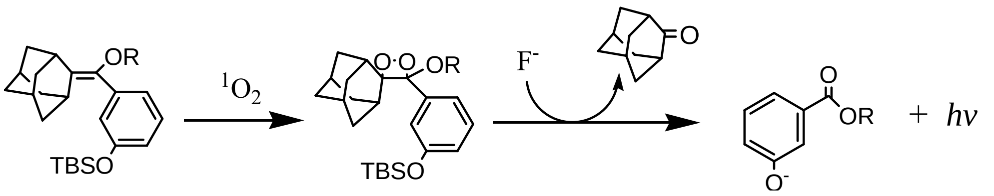


(46)

As alternative to the methods described above, Ruiz-González et al.[170] reported the synthesis and photochemical behavior study of naphthoxazole-based compounds (Table 3), that could overcome some problems related to the strong dependence on the solvent polarity or the autoxidation. On the other hand, MacManus-Spencer et al.[171] developed a trap-and-trigger method in which $^1O_2$ is trapped to form a stable dioxetane through the employment of a spiroadamantylidene- and aryloxy-substituted vinyl ether (SVE). The addition of a chemical trigger (F^-) results in the emission of visible light (reaction (48)). The evolution of the trapping reaction with the exposure time to photochemical sensitization or thermal decomposition processes and the influence of other ROS (•OH, $O_2^{-\bullet}$ and H_2O_2) present in solution were evaluated.



(48)

Finally, 4,5-dimethylthio-4'-[2-(9-anthryloxy)ethylthio]tetrathiafulvalene (TTF)[172] and tetrathiafulvalene-anthracene dyad (TTFA)[173] were synthesized in the laboratory and applied to quantify the singlet oxygen produced from the mixture H_2O_2/NaOCl, evaluating the influence of different ROS such as •OH, $O_2^{-\bullet}$ or H_2O_2 on the generation of luminescence. In spite of their high selectivity, these probes are characterized by their poor solubility.

To conclude, it has been reported that most of the probes employed to detect and quantify the concentration of singlet oxygen are not commercially available, which implies the synthesis of the trapping agents that are involved in the reaction and also the products that afterwards permit the quantitative determination. However, in spite of presenting adequate features for its application in the quantitation of $^1O_2$ such as selectivity, sensitivity, simple analytical equipment, etc., their commercial unavailability limits the accessibility and the direct applicability by other research groups. On the contrary, the use of SOSG or FFA is presented as feasible methodologies for determining the generation of $^1O_2$. Anyway, although all the papers analyzed described good selectivity and sensitivity, the scarce systems studied indicate that further research is needed not only in other AOPs to assess the viability of their use, but also in the development of an adequate probe for determining $^1O_2$.

CONCLUSIONS

ROS play a vital role in AOPs and therefore, the development of sensitive and selective methods for their detection and quantitative determination, which provide essential information for understanding the generation and reaction mechanisms of these reactive species during AOPs, is crucial. This work reports an overview of the probes and analytic techniques that have been employed by several researchers in their studies for the qualitative/quantitative identification of hydroxyl radicals, superoxide radicals and singlet oxygen, highlighting the main advantages and drawbacks associated to each methodology.

From the information presented throughout the document it can be concluded that variables such as probe choice, probe content and analytical technique are related to the expected ROS concentration and, as a result, depend on the AOP selected. Therefore, it is imperative to ensure that the selected probe is suitable under the operating work conditions. It can be expected, in a near future, further research in the design, development and/or use of new probes that overcome the limitations of the current ones in terms of selectivity, sensitivity, stability, etc., namely, gather the appropriate characteristics to approach to the ideal probe described above.

ACKNOWLEDGEMENTS

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Table 1. Main features of the probes used in the determination of •OH

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
BA: 0.1-10 mM	Fenton Electro-Fenton Photolysis	Analysis of o-, m- and p-HBA. HPLC with PDA or UV detector, fluoresecence detection or UV/vis spectrophotometry. Fluorescence detection: o-HBA, pH: 4.9; m- and p-HBA pH>11 [•OH]: 0.012- 0.9 mM	Selectivity towards •OH Repeatability and accuracy in the analysis The reaction products are stable BA is stable in presence of H_2O_2 and photochemically inert The presence of cations (Na^+,K^+,Ca^{2+},Cu^{2+},Ni^{2+}) in Fenton systems did not influence in the product concentration Results consistent with those obtained using n-propanol[73] and methanol[71] as probes	When Cl^- is present in the reaction media it acts as •OH scavenger In general, the references studied consider this method as qualitative of •OH generation pHBA can also be oxidized by •OH with a similar rate constant than BA ($k_{\bullet OH,pHBA} = 6\cdot10^9$ l/mol/s > $k_{\bullet OH,BA} = 4.3\cdot10^9$ l/mol/s) Generation of several products such as di and tri-hydroxylated BA	2, 4, 71-76
Benzene: 1.2-7 mM	Photocatalysis Electrochemical oxidation	Analysis of phenol HPLC with UV/vis detector [•OH]: 50nM, 0.1-0.23 mM	Selectivity towards •OH Easy determination of phenol Phenol formation rate > phenol oxidation rate Repeatability, especially when the withdrawn of the sample is automatized There is no direct formation of phenol under UV irradiation Negligible effect of $[NO_3^-]$ in the reaction between benzene-•OH	The presence of Cl^-, Br^- and citrate ions may result in the scavenging of •OH Benzene is highly toxic and its use is restricted in many countries The phenol stability in natural waters is just 1 h[79] The formation of other products than phenol, such as hydroquinone, catechol, resorcinol and benzoquinone was observed in electro-oxidation	77-81
3-carboxy-proxyl: 0.8 mM	Photocatalysis	Analysis of proxyl-NH EPR spectroscopy [•OH]: up to 0.25 mM	Selectivity towards •OH Simplicity Under dark conditions, TiO_2 does not affect the concentration of 3-carboxyproxyl	A fraction of 3-carboxyproxyl may react with the electrons of the conduction band leading to the formation of proxyl-OH, which implies the loss of the probe 3-carboxyproxyl may react with itself when it is irradiated Formation of several reaction products When sodium salts are present, they compete for •OH	132
3-CCA: 0.1-30 mM	γ-radiolysis and heavy ions	Analysis of 7OH-3CCA HPLC with fluorescence detection (pH 6.8) or fluorescence spectrophotometry [•OH]: Qualitative	Simple, sensitive, accurate and reproducible method Commercial availability of the probe and the product	The fluorescence is pH dependent. The analysis of the samples must be done at pH optimum that guarantees the maximum intensity In fluorescence analyses samples must be diluted to avoid filter effects on the fluorescence Formation of other hydroxylated products	112, 113

Table 1. *Continued*

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
Coumarin: 0.1-0.2 mM	Photocatalysis Fenton Electrochemical oxidation γ-radiolysis	Analysis of 7HC HPLC with fluorescence detection or fluorescence spectrophotometry [•OH]: 1.6 nM- 0.02 mM	Good selectivity towards •OH, though it may react with O_3 Sensitive and fast method Good reproducibility Good scavenger in the concentration range 10^{-3}-10^{-5} M Fluorescence only due to 7HC 7HC is a stable product and it is commercially available The direct photoelectrolysis of coumarin did not occur[103] Coumarin is not oxidized in active anodes, it requires the presence of •OH[104]	Disappearance of 7HC in the presence of O_2 y $O_2^{\bullet-}$ [6] The production of HC isomers with the hydroxyl group in the positions 3 ,4, 5, 6, 7 and 8 is likely Different values in the yield of coumarin-•OH to give 7HC are reported[41, 103, 105, 106] Photocatalysis: Slow disappearance of coumarin under UV. Besides, only dissolved •OH reacts with coumarin. At low coumarin concentration, the photocatalysis of 7HC occurs. Coumarin may cause a filter effect absorbing a fraction of the incident light[6] Photo-Fenton and electro-oxidation: reaction between 7HC and •OH[104]	6, 41, 103-111
4-CP: 1-1.72 mM	Photocatalysis Fenton	Analysis of 4CC HPLC with PDA detector [•OH]: Qualitative	Selectivity towards •OH	4CC may react also with •OH 4CP may be degraded by direct photolysis Formation of several products: 4CC, hydroquinone, benzoquinone and products derived from the ring opening	84-86
DMPO: 1-300 mM	Fenton Photocatalysis Electrochemical oxidation Sonolysis	Analysis of DMPO-OH ESR/EPR spectroscopy; LC with positive ion electrospray ionization using a tandem mass spectrometer (LC/ESI-MS/MS)[130] [•OH]: 0.2 µM- 0.15 mM	High sensitivity and reproducibility Good solubility of DMPO Short analysis time EPR analysis is not affected by the photocatalytic suspension[124] Direct photolysis of DMPO was not observed	DMSO, mannitol, Fe(II) and PO_4^{3-} present in solution act as •OH scavengers DMPO may also react with the photogenerated holes in the catalyst[122, 124] Low DMPO-OH stability: half-life of DMPO-OH is about 20 min. This compound disappears in the presence of Fe(II), PO_4^{3-} and high •OH concentration Non-selective towards •OH. Reactions with con $O_2^{\bullet-}$, $^1O_2$ and ROO• may occur	66, 67, 84, 86, 122-130

Table 1. *Continued*

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
DMSO: 5-500 mM	Fenton Photolysis Electrochemical oxidation	Analysis of HCHO-DNPH HPLC with UV detector (pH 4) [•OH]: 0.08 mM- 0.2 mM	Selectivity DMSO-•OH Good reproducibility Simple and sensitive method, easy to operate One quantitative product High solubility of DMSO and low volatility Commercial availability of DMSO and DNPH Comparison of the •OH formation rates was identical using NaTA as scavenger[42] Only 0.3-0.5% of the $\bullet CH_3$ radicals (precursor of HCHO) are consumed in the production of CH_4	Inorganic salts and other compounds present in the solution may act as scavengers The derivatization time of HCHO with DMSO requires 30 min Degradation of DMSO (C_0=1mM) and HCHO applying UV/H_2O_2 that implies an underestimation in the quantification of •OH[44]	39-44
	Fenton	Analysis of $C_{13}H_{15}O_2N$ Fluorescence spectrometry (pH 4.5) [•OH]: Qualitative	Selectivity DMSO-•OH Sensitive, simple and inexpensive method One quantitative product When the analysis of the fluorescence was carried out, it was only due to the reaction •OH	Scavenging of •OH in the presence of ascorbic acid A heating step is required (95ºC for 20 min) once all the reagents are added to the sample prior to the analysis	45
	Fenton	Analysis of o-MHA: o-methyl hydroxylamine Fluorescence spectrophotometry [•OH]: Qualitative	Fluorescence caused only by the reaction with •OH Sensitive, simple and inexpensive method One quantitative product	NN was synthesized in the laboratory In the presence of reducing agents or carbon centered radicals, o-alkoxylamine derivatives may be produced, increasing the fluorescence signal	46
	Photolysis	Analysis of the fluorescent compound generated by HPLC with fluorescence detection (pH 8) [•OH]: Qualitative	Fluorescence caused only by the reaction with •OH Method applied to fresh and sea waters under aerobic and anaerobic conditions and in the presence/absence of organic matter	The purification of aminonitroxide is needed The fluorescent product has been prepared in the laboratory In the absence of nitrate or nitrite (or in presence of organic matter) the irradiation of DMSO and nitroxide solutions may generate $\bullet CH_3$ Competition between the reaction of •OH with DMSO and nitrite in anaerobe media Competition between the reaction of $\bullet CH_3$ with O_2 and nitroxide in aerobe media	47

Table 1. *Continued*

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
DPCI: 1 mM	Sonocatalysis Photocatalysis	Analysis of DPCO UV/vis spectrophotometry [•OH]: Qualitative	The fluorescence is only caused by the oxidation of DPCI Rapid and accurate detection The required equipment is simple and the reagents are non-expensive Wide range of detection	The oxidation of DPCI to DPCO takes place through the reaction with different ROS. Different scavengers have to be added depending on the ROS studied when •OH is evaluated, 2,6-di-tert-butyl-methylphenol (BHT) was used as scavenger Oxidation-Extraction photometry method: extraction of DPCO with a mixture of benzene-CCl_4 The concentration of ROS was not quantified in these works	1, 92
FDMPO: 50 mM	Fenton	Analysis of FDMPO-OH ESR/EPR spectroscopy or nuclear magnetic resonance (NMR) [•OH]: Qualitative	Higher stability than DMPO Signal/background noise ratio higher than when DMPO is used as a probe	FDMPO was synthesized in the laboratory FDMPO reacts also with carbon centered radicals (•CH_3, •CH_2OH) The EPR spectra in the presence of $O_2^{\bullet-}$ is identical to the corresponding FDMPO-•OH	131
4-HBA 2-10 mM	Photocatalysis Electrocatalysis Fenton	Analysis of 3,4-dHBA Voltammetry[26, 65] and HPLC with UV/vis detector[23, 27] [•OH]: up to 7 mM	Selective method High sensitivity and trapping efficiency One quantitative product of importance Effective discrimination between 4HBA and 3,4-dHBA peaks during the HPLC analysis Short analysis time	CO_3^{2-} acts as scavenger of •OH Generation of oxidation intermediates during the treatment of an aqueous solution of 4HBA[23, 27] High ratio signal/background	23, 26, 27, 65
IBG: 1.1 µM	Fenton	Analysis of the chemiluminescence generated BJL analyzer with high sensitivity detector [•OH]: Qualitative	Selectivity towards •OH. The chemiluminescent product do not react with $O_2^{\bullet-}$ or H_2O_2 Rapid and specific method	It would be necessary to know the commercial availability of the chemiluminescent product generated in order to quantify the •OH concentration	121

Table 1. *Continued*

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
Methanol: 2-400 mM	Photolysis	Analysis of HCOOH-DNPH HPLC with UV detector [•OH]: 0.6 µM- 0.5 mM	Higher sensitivity compared with BA as probe. The results obtained with both probes were the same[2] Methanol is stable in presence of H_2O_2 and photochemically inert	Less efficiency in trapping •OH regarding BA[70, 71]	2, 70, 71
Ninhydrin: 22.5 mM	Fenton-like	Analysis of HO-ninhydrin Fluorescence spectrophotometry with FIA (pH 7.27) [•OH]: up to 0.02 mM	Selectivity ninhydrin-•OH Simple and fast technique (22 samples/h) Sensitive and accurate technique The presence of Na^+, K^+, NH_4^+, F^-, Cl^-, Br^-, $O_2^{\bullet-}$ did not interfere in the fluorescence intensity	An excess of ninhydrin concentration may result in fluorescence quenching and, therefore, the concentration of •OH could be underestimated	114
Nitrone: 3 mM	Fenton	Analysis of the nitroxide 2-hydroxy-2-(2-pyridyl)-3H-indol-3-on-1-oxy ESR spectroscopy (pH 7.4) [•OH]: Study of the probe viability	Commercial availability of the catalyst and reagents for the probe preparation Nitrone does not react with $O_2^{\bullet-}$	The probe was synthesized in the laboratory The efficiency of the method is limited: the utility of nitrone in the characterization of •OH is oriented to specific experimental designs Direct oxidation reaction with H_2O_2	133
NPG: 0.5 mM	Photocatalysis	Analysis oh o- and p-HNPG HPLC with PDA detector (pH 9) [•OH]: Qualitative	-	The hydroxylation reaction is pH dependent (adjusted at pH 9) Synthesis of NPG in the laboratory	95
n-propanol: 5 mM	Fenton	Analysis of propionaldehyde-DNPH HPLC with PDA detector [•OH]: up to 0.3 mM	Results consistent with those obtained using BA	The estimated yield for the reaction n-propanol-•OH to give propionaldehyde is 46% Derivatization with DNPH: 12 h	73

Table 1. *Continued*

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
OPDA: 3 mM	Photo-Fenton	Analysis of DAPN UV/vis spectrophotometry [•OH]: 0.012-0.039 mM	Good selectivity towards •OH Simple and accurate measurement	H_2O_2 may react with OPDA giving DAPN, but it was insignificant	82
p-CBA: 2-60 µM	Photocatalysis Sonocatalysis	Disappearance of p-CBA[68, 69], formation of 4-CP [5] HPLC with UV/vis detector [•OH]: Qualitative	Selectivity towards •OH Low reactivity with O_3 Non-volatile	A different product distribution is obtained depending on the AOP applied: 4-CP, hydroquinone, catechol, benzoquinone and products derived from the ring opening The concentration of 4-CP decreased with treatment time leading to an underestimation of •OH concentration[5] In presence of O_3, the degradation of p-CBA may occurs	5, 67-70
Phenol: 2.5-10 mM	Fenton Electrochemical oxidation	Analysis of pyrocatechol HPLC with EC detector [•OH]: Qualitative	Selectivity towards •OH The presence of SO_4^{2-} does not influence the degradation of phenol	Generation of several products after the reaction with •OH Formation of a polymer in dimensionally stable electrodes Br^- acts as scavenger of •OH and the presence of Cl^- implies the formation of active chlorine and chloride species that participate in the oxidation process	137, 138
Phenylalanine 20 mM	Fenton	Analysis of o-, m- and p-tyrosine HPLC with UV detector and LC-MS [•OH]: Qualitative	Time analysis lower than 6 min Additional LC-MS allows the discrimination and identification of the signal generated by each product	Generation of several products	94

Table 1. *Continued*

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
Phth: 0.1-4 mM	Fenton Electrochemical methods	Analysis of 5OH-Phth and 6OH-Phth Chemiluminescence analysis in a PMT, luminometer or HPLC-UV followed by a luminometer (pH 4.5-9.5) [•OH]: 1.5 μM-1 mM	Selectivity towards •OH Phth is not oxidized by HO_2•, HO^-, SO_4^{2-}, Co(III) or Ce(IV). There is no influence of transition metals in the pH region 4.5-9.5 Sensitive and reproducible method Stability of the oxidation products Good solubility of Phth at neutral and alkaline pH Phth does not produce background chemiluminescence A separation stage was not required[119] prior to the analysis in a Fenton-like system (Cu(II)) The product distribution is not dependent of Fe(III) or Cu(II) when these are lower than 1mM	Br^-, Na_2CO_3 and organics act as scavengers of •OH H_2O_2 concentration higher than 0.15 mM and DTPA/EDTA ratio greater than 0.10 mM may interfere in the analysis (106) Generation of several products, other than 5OH-Phth and 6OH-Phth Luminescence emission of 5OH-Phth is 40 times higher than 6OH-Phth, which could result in an underestimation of •OH concentration The chemiluminescence is pH dependent A prior HPLC stage to separate the oxidation products is very useful	117-119, 134
Pyrocatechol: 2.5 mM	Fenton	Analysis of pryogallic acid HPLC with EC detector [•OH]: Qualitative	Selectivity towards •OH	-	137
Quinoline: 0.15-0.95 mM	Fenton Photocatalysis	Quantification of all the identified products HPLC with PDA detector and GC-MS [•OH]: Qualitative	Easiness in the identification of the reaction of quinoline with •OH or other ROS Good stability of quinoline The oxidation products have at least one aromatic ring that allows their easy detection by HPLC-UV or GC-MS The product distribution is not affected by steric impediments The solubility of quinoline is high enough to let an appropriate initial quinoline concentration for trapping all the generated •OH Quinoline is moderately polar and basic which prevents the degradation influenced by ionic associations	Quinoline reacts with $O_2^{\bullet-}$, which is favored at high pH In photocatalysis, the use of both analytical techniques, HPLC and GC-MS, is required because one of the products (8-hydroxyquinoline) does not elute correctly by HPLC[87] Generation of several products, whose distribution depends on the specie with which quinoline reacts Synthesis in the laboratory of all the identified products	87, 88

Table 1. *Continued*

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
RhB: 0.2 mM	Fenton	Analysis of the absorbance of RhB UV/vis spectrophotometry [•OH]: Qualitative	Simple and cost-effective method Reproducibility RhB is not oxidized by H_2O_2	In Fenton system, the concentration of RhB diminishes slightly due to the absorption on Fe(II)	93
RNO: 1.5-67 µM	Photocatalysis Electrochemical oxidation	Analysis of RNO decrease UV/vis spectrophotometry (pH 6-12) [•OH]: $4.17 \cdot 10^{-13}$ M	RNO does not react with $^1O_2$, $O_2^{\bullet-}$ or other peroxy compounds	RNO is oxidized by O_3, Cl_2, HClO and ClO^- In photocatalysis, and in the absence of O_2, RNO is reduced by the generated electrons In active anodes (Ti/Pt and Ti/RuO_2), RNO may be oxidized by the O_2 adsorbed on the anode Analysis at pH 6-12 to avoid the protonated specie that results in an absorbance diminishment	33, 89-91
$Ru(bpy)_3^{2+}$: 0.5 mM	Fenton	Analysis of the chemiluminescence of the excited $Ru(bpy)_3^{2+}$ FIA with EC detector [•OH]: Qualitative	Selectivity towards •OH Accurate method Processing of 80 samples/h	$Ru(bpy)_3^{3+}$ is unstable in aqueous solution. Its preparation is carried out in an electrochemical reactor from $Ru(bpy)_3^{2+}$ prior the detector Antioxidant compounds such as ascorbic and gallic acid act as scavengers of •OH	120
$Ru(NH_3)_6^{3+}$: 5 mM	Fenton Photolysis	$Ru(NH_3)_6^{3+}/Ru(NH_3)_6^{2+}$ CV and CA [•OH]: $9.1 \cdot 10^{-12}$-$9.5 \cdot 10^{-11}$ M	Results consistent with those obtained with SA as a probe by HPLC analysis ROO• and $O_2^{\bullet-}$ do not interfere in the analysis	CV analysis: recommended when the uncovered electrode surface ranges between 2-70% CA analysis: Recommended when the uncovered electrode surface is lower than 2% In the presence of $KMnO_4$ the analytical signal increases	24

Table 1. *Continued*

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
SA: 0.2-10.9 mM	Fenton Photocatalysis Sonocatalysis Hydrodynamic cavitation Electrochemical technologies	2,3-dHBA and 2,5-dHBA HPLC-ECD (pH 7.4), HPLC-UV (pH 2), HPLC-PDA or HPLC-fluorescence (pH 5.9), capillary electrophoresis (pH 2.8 or 7.4), UV spectrophotometry [•OH]: 0.25 μM- 6.5 mM	Selectivity SA-•OH Sensitivity, reproducibility and repeatability Stability of the products Solubility of SA in water Good chromatographic separation There is no SA concentration change, when irradiated in the presence of TiO_2/SiO_2 Electrophoresis requires lower sample volume and cheaper instrumentation, shows higher efficiency and higher reproducibility, and is faster than HPLC Results consistent with those obtained with an electrochemical sensor[24]	The presence of DMSO, mannitol or other organics result in the scavenging of •OH The optimum concentration of SA to obtain a high efficiency in the capture of •OH is different based on the AOP An excess of SA is recommended, avoiding solubility limitations Importance of the SA/2,5-dHBA ratio because of their similar hydroxylation kinetic constant[24] Production of several products, including catechol and hydroquinone Capillary electrophoresis requires specific pH for the proper separation of reagents and products[174] The mineralization process results in low reliability when electrochemical oxidation or electro-Fenton are applied	24, 38, 51-64, 126, 135, 136, 174
SCN^{-}: 100 μM	Radiolysis	Analysis of $(SCN)_2^{\bullet -}$ [•OH]: Qualitative	The results obtained for the kinetic constant are consistent with those observed by monitoring the evolution of dissolved organic carbon (DOC)	-	83
TA and NaTA: 0.01-75 mM	Fenton Photocatalysis Sonolysis Electrochemical methods	Analysis of OHTA HPLC-UV/vis (pH 3), HPLC-fluorescence (pH 2.8 or 4.37) , fluorescence spectrophotometry (pH 6-11) [•OH]: 0.31-30 μM	High sensitivity Rapid and simple technique One quantitative product Fluorescence stability of OHTA lasts 24 h The UV analysis is possible at OHTA concentration higher than 1 mM NaTA presents lower solubility limitations than TA Good correlation between the results obtained by HPLC (TA), ESR (DMPO)[99] and HPLC (DMSO)[42] FIA allows the simple, fast ,accurate and automatic determination of the fluorescence	The reaction TA-•OH is affected by the solution pH Reaction of TA with $O_2^{\bullet -}$ and H_2O_2 The presence of inorganic salts and organics result in •OH scavenging An excess of NaTA may quench the fluorescence Later oxidation, deprotonation or photolytic reactions are possible The chemical yield of TA-•OH is estimated around 80% Solubility limitations of TA Photocatalysis: TA reacts only with dissolved •OH Photolytic degradation of OHTA OHTA has a higher hydroxylation kinetic rate constant value than TACarboxylic acids produced along the photocatalysis of TA (0.12-0.60 mM)[116]	25, 29, 42, 65, 96-102, 115, 116

Table 2. Main features of the probes used in the determination of $O_2^{\bullet-}/HO_2^{\bullet}$

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
BA: 1 mM	Fenton system	Analysis of OHBA Fluorimetry (pH 11) $[O_2^{\bullet-}]$: 1 nM-3.1 µM	High sensitivity and easy calibration	Formation of numerous products: hydroxybenzene isomers and decarboxylated products The fluorescence signal could be increased by the impurities present in solution or diminished by competitive reactions Less sensitivity than NaTA[150] Specific experimental setup	150-152
FC: 40 µM	Thermal decomposition	Analysis of the absorbance at a wavelength of 550 nm UV spectrophotometry $[O_2^{\bullet-}]$: 9 µM	Selectivity Insignificant extent of the reaction with H_2O_2 when its concentration is lower than < 0.1mM	FC reduction and oxidation by Cu and Mn species that implies an underestimation of $O_2^{-\bullet}$	141
Luminol: 40 µM- 7 mM	Fenton Photocatalysis Cyclic voltammetry	Analysis of the chemiluminescence generated Photon counting system with photomultiplier tube (pH 9-11) $[O_2^{\bullet-}]$: $3.9 \cdot 10^{-15}$-$1.8 \cdot 10^{-4}$ M	When photocatalysis is applied, the subsequent addition of luminol prevents its reaction with the photocatalyst	Luminol is not selective. It also reacts with H_2O_2 and other species including trace metals such as Co, Cu, Mn, Cr, Mg, Fe and certain complex of these metals, $N_3^{\bullet}$, $CO_3^{-\bullet}$, SCN^{-}, I^{-}, Br^{-}, $Br_2^{-\bullet}$ and ClO_2 Luminol produces background noise during their luminescence analysis and its detection is restricted to alkaline pH	100, 101, 134, 142-147, 175
MCLA: 1-350 µM	Photocatalysis Cyclic voltammetry Thermal decomposition	Analysis of the chemiluminescence generated Photon counting system with photomultiplier tube $[O_2^{\bullet-}]$: 25-60 nM	Selective towards $O_2^{-\bullet}/HO_2^{\bullet}$ and $^1O_2$. •OH and H_2O_2 do not interfere in the analysis High sensitivity The method allows the quantification of $O_2^{-\bullet}/HO_2^{\bullet}$ at any pH	$O_2^{-\bullet}$ may react with buffer solutions containing amines Background chemiluminescence owing to the auto-oxidation of MCLA When pH<pKa=7.75, the chemiluminescence decreases	107, 134, 141, 143

Table 2. *Continued*

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
NaTA: 1 mM	Fenton system	Analysis of OHTA Fluorimetry (pH 11) $[O_2^{\bullet -}]$: Up to 5 µM	TA is more sensitive than BA	The half-life of $O_2^{-\bullet}/HO_2^{\bullet}$ depends on pH Specific experimental setup	150
NBD-Cl: 100 µM	Thermal decomposition	Analysis of the absorbance of the generated product UV spectrophotometry $[O_2^{\bullet -}]$: 20 µM	-	NBD-Cl may react with amino acids, amines, thiols, ketyl and alkoxyl radicals	141
NBT: 0.2-1 mM	Photocatalysis	Analysis of the absorbance of NBT or NBT-formazan UV-vis spectrophotometry $[O_2^{\bullet -}]$: Up to 0.17 mM	NBT does not react with •OH or H_2O_2 NBT does not react with TiO_2	Negligible formation of $O_2^{-\bullet}/HO_2^{\bullet}$ under a N_2 atmosphere 2-propanol scavenges $O_2^{-\bullet}$ Low water solubility of NBT	68, 148, 149
XTT: 0.1 mM	Photocatalysis	Analysis of the absorbance of XTT-formazan UV-vis spectrophotometry $[O_2^{\bullet -}]$: 2.5 nM	Good selectivity High solubility of XTT in water, especially compared with NBT	-	68, 90

Table 3. Main features of the probes used in the determination of $^1O_2$

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
AAPD: 0.5-5 µM	Fenton-like	Analysis of the generated fluorescence Fluorescence spectrophotometry [$^1O_2$]: Qualitative	Selectivity towards $^1O_2$ High sensitivity	The probe is synthesized in the laboratory	165
Direct analysis	Photocatalysis	Monitoring of $^1O_2$ phosphorescence Photon-counting system with photomultiplier [$^1O_2$]: Up to 4.7 µM	Direct measurement	Under N_2 environments, the concentration of $^1O_2$ decreases, highlighting the importance of O_2 in its generation Methionine and folic acid act as $^1O_2$ scavenges The reaction with $O_2^{\bullet -}$ may deactivate $^1O_2$	160-162
DMAX: 10 µM	Thermal decomposition	Analysis of the fluorescence: formation of a fluorescent product Fluorescence spectrophotometry (pH 7.4) [$^1O_2$]: Qualitative	The reaction rate between $^1O_2$ and DMAX is higher than with DPAX Sensitivity of DMAX is 53-fold higher than that of DPAX Hydrophobicity of DMAX is less than that of DPAX Initial DMAX complex hardly emits fluorescence	DMAX is synthesized in the laboratory and. numerous steps are required	167
DPAX: 1 µM	Fenton-like	Analysis of the fluorescence: formation of a fluorescent product Fluorescence spectrophotometry [$^1O_2$]: Qualitative	Good selectivity towards $^1O_2$ Useful probe in basic and neutral aqueous solutions	DPAX is synthesized in the laboratory Fluorescence sharply decreases at acidic pH	166
FFA: 0.1-0.2 mM	Photocatalysis	Analysis of FFA decrease HPLC (pH 7) [$^1O_2$]: $6.7\cdot10^{-14}$-$1.8\cdot10^{-4}$ M	Good selectivity towards $^1O_2$ The reaction with $O_2^{\bullet -}$ becomes important at FFA concentrations higher than 10mM FFA concentration does not decrease under either irradiation or dark conditions, or presence of NaCl	O_2 and a sensitizer are essential in the production of $^1O_2$ N_3^- quenches $^1O_2$	68, 164

Table 3. *Continued*

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
MTTA-Eu^{3+}: 10 µM	Fenton-like	Analysis of the fluorescence: formation of a fluorescent product Fluorescence spectrophotometry [$^1O_2$]: Qualitative	Good selectivity and sensitivity towards $^1O_2$ High solubility of the probe in water The probe allows the work in a wide pH range Formation of a product with large fluorescence time Initial Eu (III) complex hardly emits fluorescence	Europium (III) complex is synthesized in the laboratory	168
Naphthoxazole-based:	Photo-sensitization	Analysis of the fluorescence: formation of a fluorescent product Fluorescence spectrophotometry [$^1O_2$]: Study of the probe viability	Good selectivity towards $^1O_2$ Negligible effects of self-sensitization Fluorescence enhancement factors up to 300-fold	The probe is synthesized in the laboratory	170
PATA-Tb^{3+}: 0.02-10 µM	Fenton-like	Analysis of the luminescence: formation of a luminescent product Luminescence spectrophotometry (pH 10.5) [$^1O_2$]: 6.8 µM	Good selectivity and sensitivity towards $^1O_2$ High solubility of the probe in water The probe allows the work in a wide pH range Formation of a product with large fluorescence time The possibility of working under time-resolved fluorescence mode lets the removal of fluorescence background Initial Tb(III) complex hardly emit fluorescence	Terbium chelate is synthesized in the laboratory	169
Re(I) complex: 2.8 mM	Fenton-like	Analysis of the luminescence: formation of a luminescent product Luminescence and UV/vis spectrophotometry [$^1O_2$]: Up to 40 mM	High selectivity and sensitivity towards $^1O_2$ Detection limit lower than other chemiluminescent methodologies and comparable with the probes based on Eu(III) y Tb(III) Re(I) may be excited under visible light Re(I) complex hardly emits fluorescence	Synthesis of the Re complex in the laboratory	153

Table 1. *Continued*

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
SA: 0.2-10.9 mM	Fenton Photocatalysis Sonocatalysis Hydrodynamic cavitation Electrochemical technologies	2,3-dHBA and 2,5-dHBA HPLC-ECD (pH 7.4), HPLC-UV (pH 2), HPLC-PDA or HPLC-fluorescence (pH 5.9), capillary electrophoresis (pH 2.8 or 7.4), UV spectrophotometry [•OH]: 0.25 μM- 6.5 mM	Selectivity SA-•OH Sensitivity, reproducibility and repeatability Stability of the products Solubility of SA in water Good chromatographic separation There is no SA concentration change, when irradiated in the presence of TiO_2/SiO_2 Electrophoresis requires lower sample volume and cheaper instrumentation, shows higher efficiency and higher reproducibility, and is faster than HPLC Results consistent with those obtained with an electrochemical sensor[24]	The presence of DMSO, mannitol or other organics result in the scavenging of •OH The optimum concentration of SA to obtain a high efficiency in the capture of •OH is different based on the AOP An excess of SA is recommended, avoiding solubility limitations Importance of the SA/2,5-dHBA ratio because of their similar hydroxylation kinetic constant[24] Production of several products, including catechol and hydroquinone Capillary electrophoresis requires specific pH for the proper separation of reagents and products[174] The mineralization process results in low reliability when electrochemical oxidation or electro-Fenton are applied	24, 38, 51-64, 126, 135, 136, 174
SCN^{-}: 100 μM	Radiolysis	Analysis of $(SCN)_2^{\bullet -}$ [•OH]: Qualitative	The results obtained for the kinetic constant are consistent with those observed by monitoring the evolution of dissolved organic carbon (DOC)	-	83
TA and NaTA: 0.01-75 mM	Fenton Photocatalysis Sonolysis Electrochemical methods	Analysis of OHTA HPLC-UV/vis (pH 3), HPLC-fluorescence (pH 2.8 or 4.37) , fluorescence spectrophotometry (pH 6-11) [•OH]: 0.31-30 μM	High sensitivity Rapid and simple technique One quantitative product Fluorescence stability of OHTA lasts 24 h The UV analysis is possible at OHTA concentration higher than 1 mM NaTA presents lower solubility limitations than TA Good correlation between the results obtained by HPLC (TA), ESR (DMPO)[99] and HPLC (DMSO)[42] FIA allows the simple, fast ,accurate and automatic determination of the fluorescence	The reaction TA-•OH is affected by the solution pH Reaction of TA with $O_2^{\bullet -}$ and H_2O_2 The presence of inorganic salts and organics result in •OH scavenging An excess of NaTA may quench the fluorescence Later oxidation, deprotonation or photolytic reactions are possible The chemical yield of TA-•OH is estimated around 80% Solubility limitations of TA Photocatalysis: TA reacts only with dissolved •OH Photolytic degradation of OHTA OHTA has a higher hydroxylation kinetic rate constant value than TACarboxylic acids produced along the photocatalysis of TA (0.12-0.60 mM)[116]	25, 29, 42, 65, 96-102, 115, 116