

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

Pablo Fernández-Castro, Marta Vallejo, M^a Fresnedo San Román, Inmaculada Ortiz*

Department of Chemical and Biomolecular Engineering, ETSIIyT, University of Cantabria, Avda. Los Castros s/n, 39005 Santander, Spain

* Correspondence to: I. Ortiz, Department of Chemical and Biomolecular Engineering, ETSIIyT, University of Cantabria, Avda. Los Castros s/n, 39005 Santander, Spain. E-mail: ortizi@unican.es, Phone: +34 942 201585

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

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/jctb.4634

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

HO₂[•]: 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-Eu³⁺: [4'-(10-methyl-9-anthryl)-2,2':6',2''-terpyridine-6,6''-diyl]bis(methylenenitrilo)tetrakis(acetate)-Eu³⁺

NaTA: sodium terephthalate

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

NBT: nitroblue tetrazolium salt

Nitron 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

¹O₂: singlet oxygen

O₂^{•-}: 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-Tb³⁺: N,N,N',N'-[2,6-bis(3'-aminomethyl-1'-pyrazolyl)-4-(9''-anthryl)pyridine] tetrakis (acetate)-Tb³⁺

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)₃²⁺: tris(2,2'-bipyridin)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: 4,3-dimethylthio-4'-[2-(9-anthryloxy)ethylthio]tetrathiafulvalene

TTFA: tetrathiafulvalene-anthracene dyad

XTT: 2,3-bis(2-methoxy-4-nitro-5-sulphophenyl)-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 ($\bullet\text{OH}$), superoxide radical ($\text{O}_2^{\bullet-}$) and hydroperoxyl radical (HO_2^{\bullet}), but also non-radicals such as singlet oxygen ($^1\text{O}_2$) 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 $\bullet\text{OH}$ 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 wastewaters⁷ 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 $\bullet\text{OH}$)^{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. Bartosz³⁰ 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

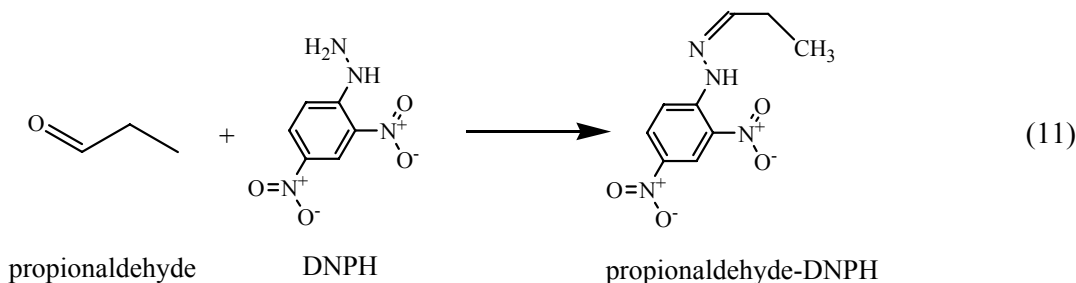
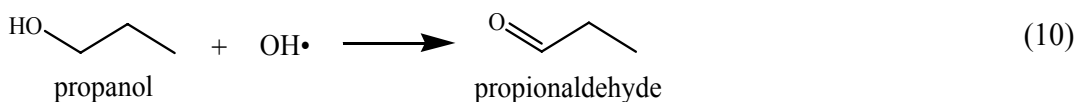
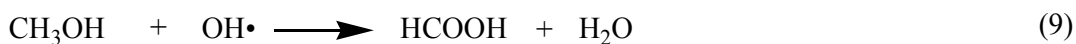
ROS are relatively short-lived molecules that contain oxygen atoms.^{28,33-35} The radical ROS ($O_2^{\cdot-}$, HO_2^{\cdot} and $\cdot OH$) differ from the molecules (H_2O_2 and 1O_2) in the unpaired electrons that confer them higher reactivity. Regardless of the nature of ROS, it is essential to take 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 $\cdot OH$, $O_2^{\cdot-}/HO_2^{\cdot}$ and 1O_2 .

Hydroxyl radical

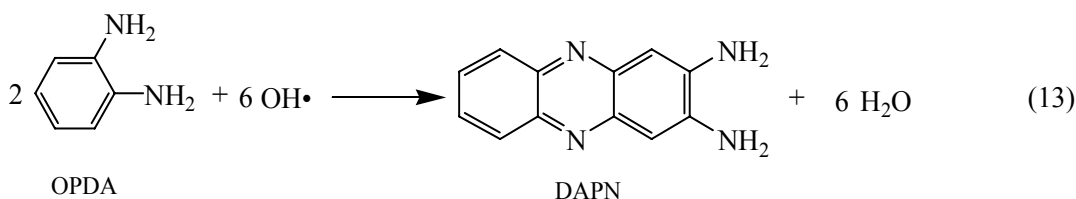
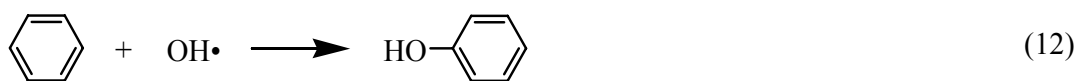
$\cdot OH$ is the most reactive oxygen radical with a very high standard potential, $E^\circ(\cdot OH, H^+/H_2O)$, of 2.18 V vs. the normal hydrogen electrode (NHE) at pH 7.^{28,37,38} $\cdot OH$ plays an important role in the degradation of organic compounds in natural waters owing to its high and non-specific 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 $\cdot OH$ formed in AOPs of aqueous systems are detailed.

Absorbance probing methods

Absorbance probing methods are the most commonly used in the assessment of $\cdot OH$ 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.



Benzene has been also used as $\cdot\text{OH}$ trapping in Fenton and photocatalytic processes allowing the measurement of $\cdot\text{OH}$ concentration through the formation of phenol (reaction (12)) in different systems such as Fe(III)-citrate,⁷⁷ Fe(III)-pyruvate,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-phenyldiamine (OPDA), was used by Fang et al.⁸² as probe for quantitatively identifying the amount of $\cdot\text{OH}$ generated in photo-Fenton through the quantification of the reaction product 2,3-diaminophenazine (DAPN) (reaction (13)). This probe displayed a good selectivity towards $\cdot\text{OH}$ with a simple analytical method.

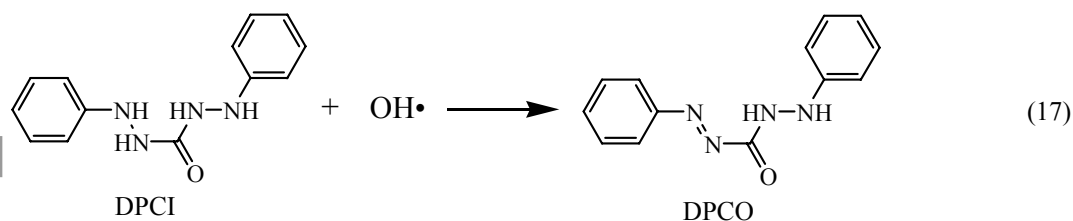
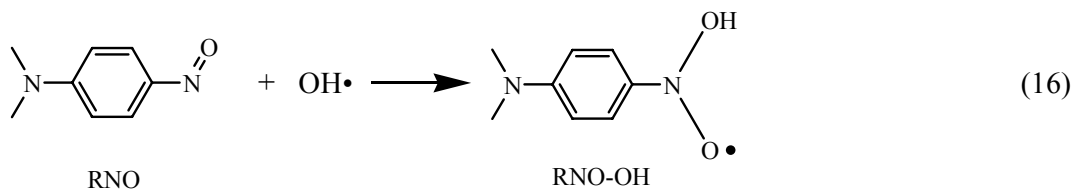


One more molecular probe applied to determine the kinetic rate constant of $\cdot\text{OH}$ generation during radiolysis of natural waters is SCN^- , through competitive kinetics with DOM (reactions (14) and (15)).⁸³

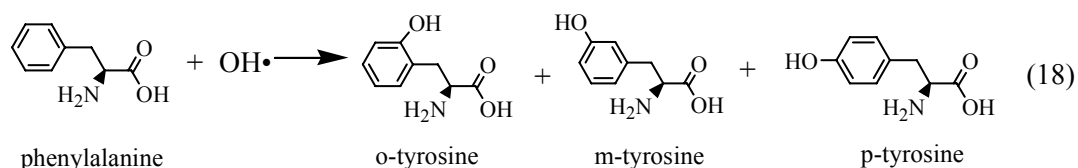


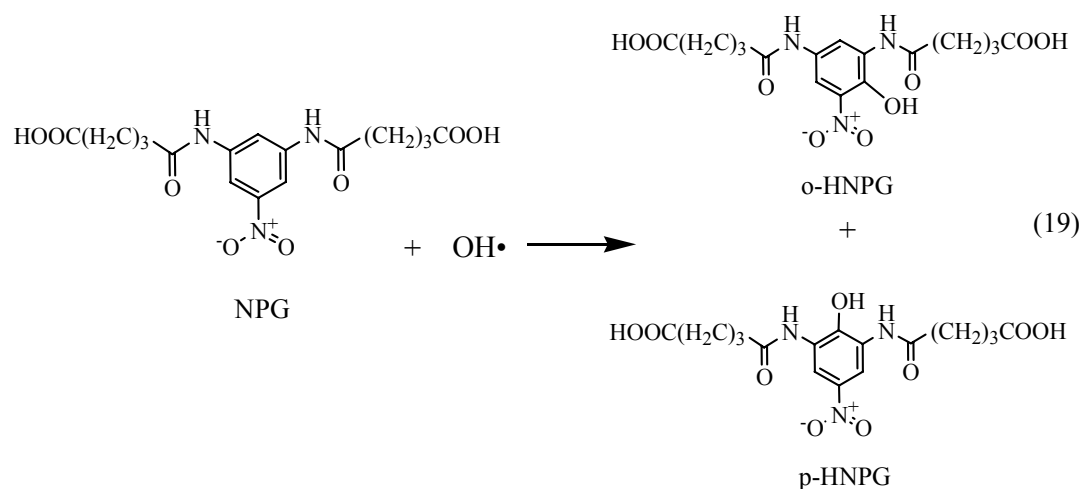


On the other hand, there are some probes that have been used with the purpose of quantifying the formation of $\cdot\text{OH}$ but are not advisable because they are not selective in the assessment of $\cdot\text{OH}$. On this sense, the use of 4-chlorophenol (4-CP) led to the generation of numerous products of quantification, in addition to 4chlorocatechol (4CC), which in turn were further oxidized in Fenton,⁸⁴ photolytic⁸⁵ 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.



Though not directly related to the quantitative/qualitative $\cdot\text{OH}$ determination, some of these molecular probes mentioned above such as 4-HBA,⁶⁵ BA⁴ 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 isomers⁹⁵ (HNPG, reaction (19)).

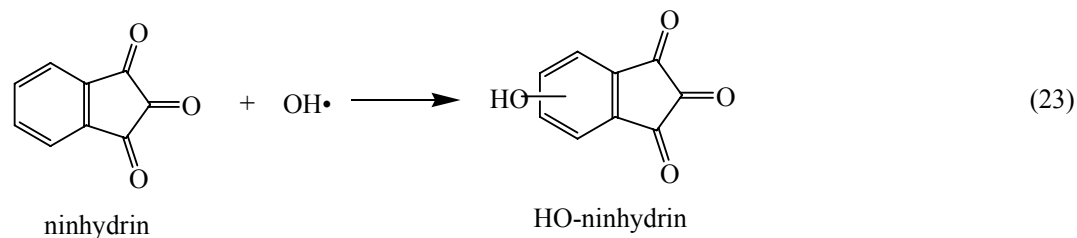
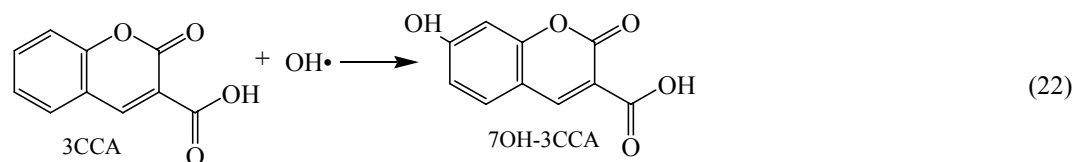
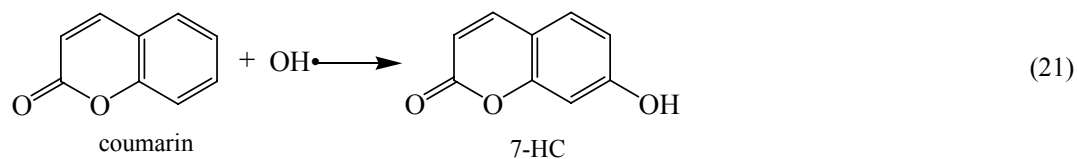
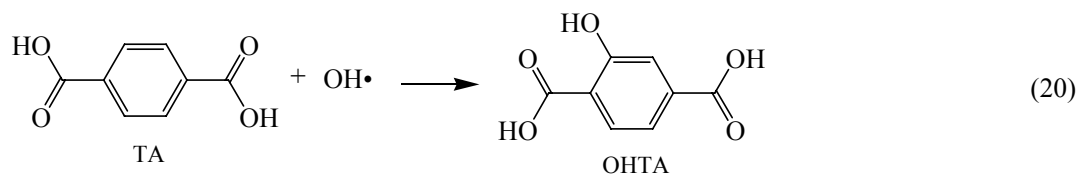




Fluorescence probing methods

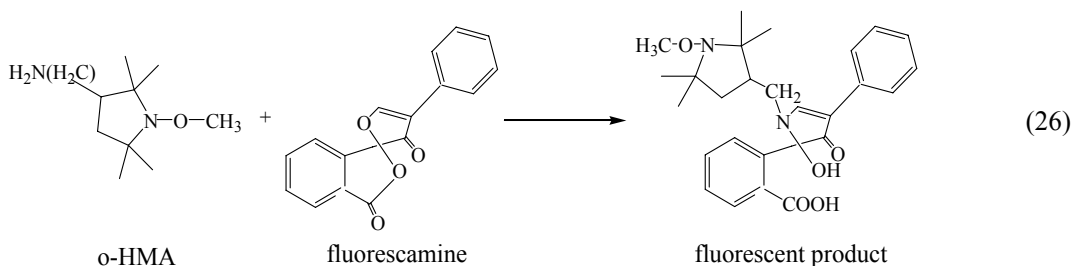
The basis of a fluorescence probing method consists on the appearance of a fluorescence product after the reaction of the molecular probe with $\cdot\text{OH}$. The excitation of the reaction product at a specified wavelength results in the emission of fluorescence which is then recorded and translated 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 $\cdot\text{OH}$ 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



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 $\cdot\text{OH}$ 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 $\cdot\text{OH}$ in Fenton^{45,46} and photochemical⁴⁷ 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 $\cdot\text{OH}$ through reactions (1)-(3), with 1,3-cyclohexanedione (CHD) and ammonium according to reaction (24), where the fluorescence emitted by $\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}$ 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

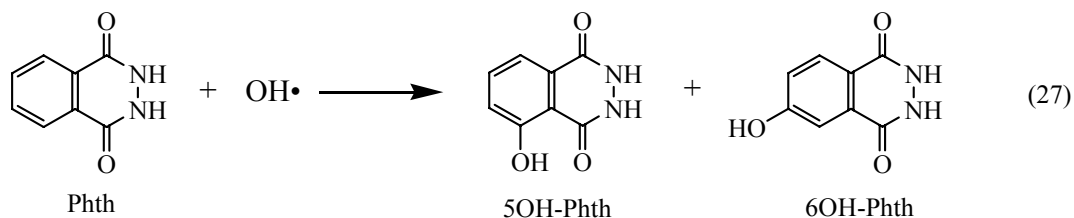
during the derivatization process or the addition of an additional compound (NN) which has to be synthesized in the laboratory.



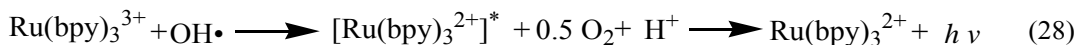
Chemiluminescence probing methods

In chemiluminescence probing methods, the reaction between a chemiluminogenic compound and $\cdot\text{OH}$ 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 $\cdot\text{OH}$ 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 $\cdot\text{OH}$ 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 $\cdot\text{OH}$ concentration.

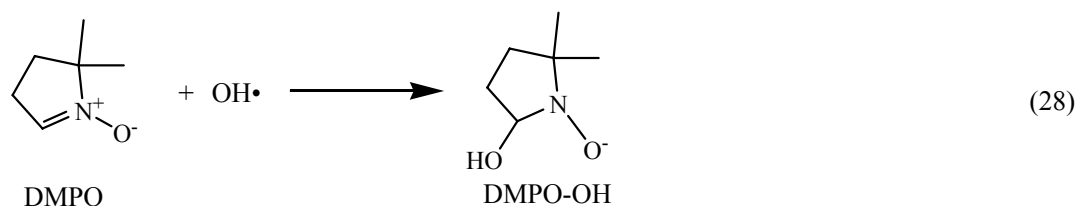


Two additional probes, tris(2,2'-bipyridine)ruthenium (III) ($\text{Ru}(\text{bpy})_3^{2+}$, reaction (28))¹²⁰ and Indoxyl- β -glucuronide (IBG)¹²¹ were used to qualitatively characterize the scavenging capacity of different antioxidants through the chemiluminescence produced in a Fenton process. Despite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

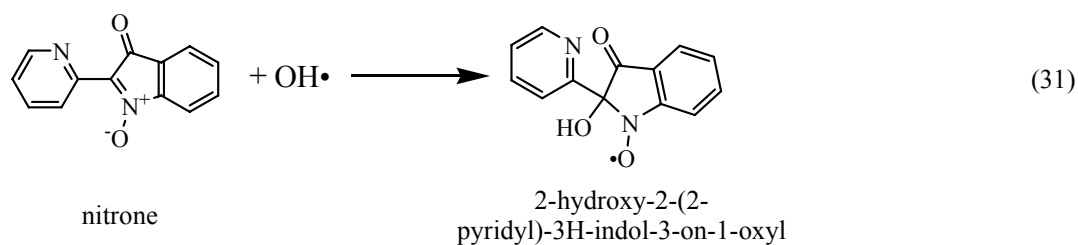
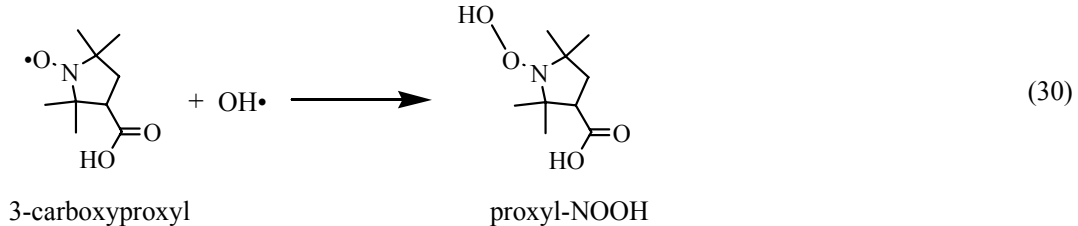
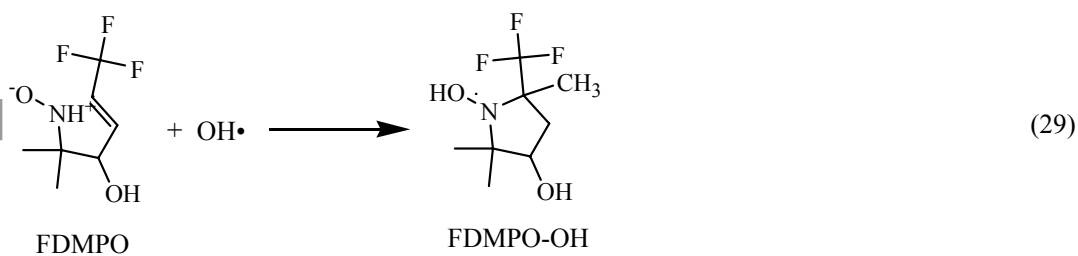


Spin-trapping methods

One of the oldest techniques in the determination of $\bullet\text{OH}$ is the spin-trapping method, which usually involves organic nitrene or nitroso compounds that after the reaction with $\bullet\text{OH}$ 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 nitrene) belong to this group. DMPO is, perhaps, the spin trap and one of the probes most used for the quantitative determination of the $\bullet\text{OH}$ 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 Fenton¹²⁴ 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} Fenton¹²⁵⁻¹²⁸ and photocatalysis⁸⁴ 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 compounds¹³⁰ 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 $\text{O}_2^{\bullet-}$, $^1\text{O}_2$ and $\text{ROO}\bullet$.

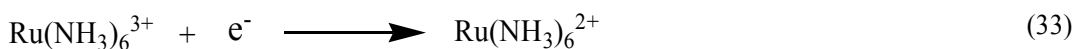
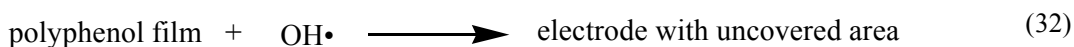


Additionally, FDMPO, a variety of DMPO, was synthesized in the laboratory for the viability study of its use as spin-trapping agent in the detection of free radicals such as $\bullet\text{OH}$ (reaction (29)), $\bullet\text{CH}_3$ and $\bullet\text{CH}_2\text{OH}$ in a Fenton system,¹³¹ although no quantitative results related to the concentration or generation rate of $\bullet\text{OH}$ were presented. FDMPO displayed higher stability than DMPO but it was also non-selective towards $\bullet\text{OH}$. On the other hand, the spectroscopic measurement of proxyl-NOOH, produced from the reaction of 3-carboxyproxyl with $\bullet\text{OH}$ (reaction (30)), was carried out to quantify the $\bullet\text{OH}$ 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, nitron (synthesized in the laboratory) was also employed as probe in the determination of $\bullet\text{OH}$, although its efficiency to spin trap these radicals was limited (reaction (31)).¹³³

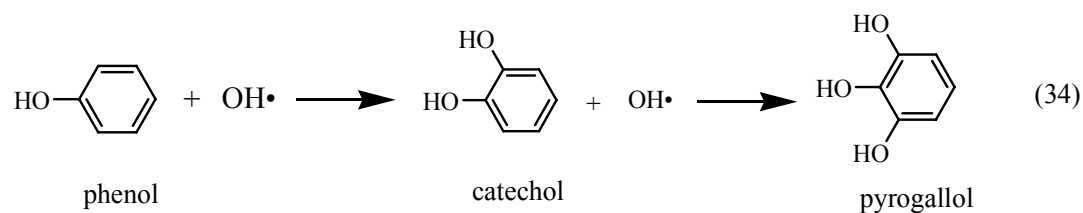


Electrochemical analyses

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 $\bullet\text{OH}$ 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 $\bullet\text{OH}$. In a different work, Gualandi and Tonelli²⁴ used an electrode covered by a polyphenol film and the redox pair $\text{Ru}(\text{NH}_3)_6^{3+}/\text{Ru}(\text{NH}_3)_6^{2+}$. The relationship between the uncovered area (reaction (32)), as consequence of the reaction between the polyphenol film and the $\bullet\text{OH}$ produced in Fenton and photocatalysis processes, and the concentration of $\bullet\text{OH}$ was established through the chromatographic method using SA. Once this relationship was known, the $\bullet\text{OH}$ 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 $\text{Ru}(\text{NH}_3)_6^{3+}$ (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 $\bullet\text{OH}$ generated.



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 $\bullet\text{OH}$ by electrochemical analyses in Fenton treatment. Nevertheless, after 5 minutes of Fenton process or when electrochemical oxidation was applied¹³⁸ the degradation of phenol and its oxidation intermediates were observed (reaction (34)) resulting in an underestimation of $\bullet\text{OH}$ concentration.

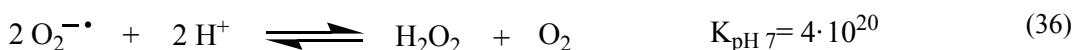


As a summary of the reviewed information regarding the analysis of $\bullet\text{OH}$, some requisites, obviating the analytical equipment requirements, that must be taken into account in the selection of the adequate molecular probe include: (1) the selectivity of the selected probe where organic compounds such as benzoic acid and related compounds, 3-CCA, DMSO, phenol, SA and TA/NaTA displayed high selectivity towards $\bullet\text{OH}$, whereas DMPO, nitron and DPCI present the lowest selectivity; (2) the stability of the quantifiable compound, where DMPO and 3-carboxypropyl 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.

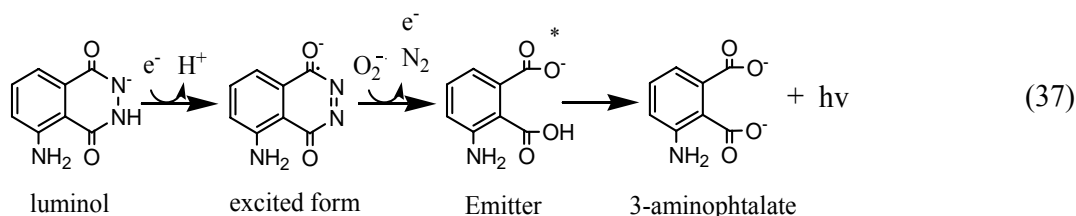
Superoxide and hydroperoxyl radical

$\text{O}_2^{\bullet -}$ is produced as a result of the donation of an electron to oxygen,³⁷ and its protonation leads to $\text{HO}_2\cdot$, although in aqueous media $\text{O}_2^{\bullet -}$ predominates over $\text{HO}_2\cdot$ ^{28,139} (reaction (35)). Though $\text{O}_2^{\bullet -}$ 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, $E^\circ(\text{O}_2^{\bullet -}, \text{H}^+/\text{H}_2\text{O}_2) = 0.95 \text{ V vs. NHE at pH} = 7$, is less than half of the corresponding to $\bullet\text{OH}$. The second-order rate

constants are not as high as in the case of $\bullet\text{OH}$ reaction, but they can reach the range 10^7 - $10^{10} \text{ M}^{-1}\text{s}^{-1}$ when $\text{O}_2^{\bullet-}$ reacts with luminol, superoxide dismutase (SOD), different quinones, etc.¹³⁹ Direct measurement of $\text{O}_2^{\bullet-}$ 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 $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$.¹⁴¹ The main advantages and limitations described by the authors of the analyzed literature are summarized in Table 2.



The most used probe for the quantitative determination of $\text{O}_2^{\bullet-}$ is luminol, leading to the generation of chemiluminescence (reaction (37)) that is then measured by a luminometer. This method has been applied to measure $\text{O}_2^{\bullet-}$ concentration in Fenton systems.¹⁴² In addition, the concentration of $\text{O}_2^{\bullet-}$ 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 $\text{O}_2^{\bullet-}$ produced;^{101,145,146} monitoring and differentiation, with a time-resolved technique, of the luminescence generated by the reaction of luminol with $\text{O}_2^{\bullet-}$ or with H_2O_2 ;^{145,147} and generation and deactivation study of $\text{O}_2^{\bullet-}$ on the TiO_2 surface.¹⁴⁵ Nevertheless, luminol presents important weaknesses as its non-selectivity towards $\text{O}_2^{\bullet-}$ and the background noise during the luminescence analyses which restrict its use to alkaline pH.



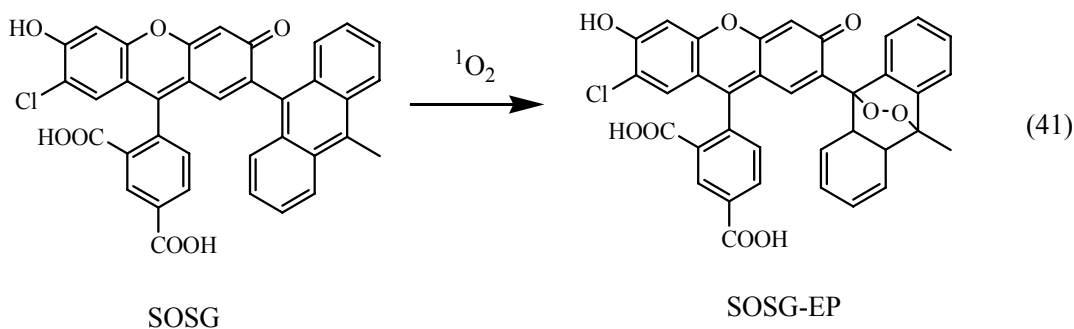
The methoxy cypiridina luciferin analog (MCLA) is another molecular probe used in the indirect determination of $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ by a chemiluminescent method. The progress of the concentration of $\text{O}_2^{\bullet-}$

Singlet oxygen

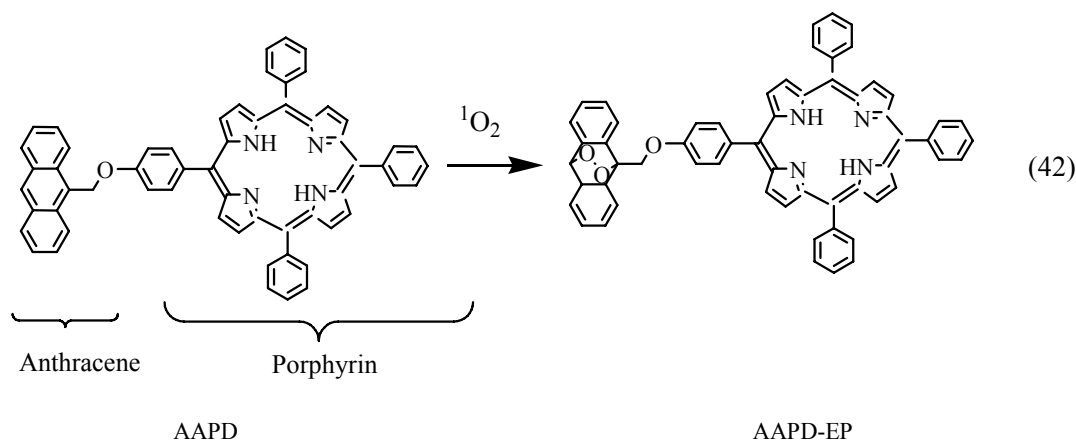
$^1\text{O}_2$, the lowest excited state of molecular oxygen, can be used as a highly active oxidant in chemical, biological and environmental systems.^{37,153,154} $^1\text{O}_2$ can be easily generated in solution by energy transfer from excited photosensitizers or chemically, which are the most common procedures.^{28,154-157} $^1\text{O}_2$ has a standard potential $E^\circ(^1\text{O}_2/\text{O}_2^-)$ 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 $^1\text{O}_2$ has been carried out at 1270 nm, although sometimes the weak signal recorded hinders the application of this direct analytical method.^{158,159} The research group of Daimon¹⁶⁰⁻¹⁶² studied the production of $^1\text{O}_2$ 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 $^1\text{O}_2$. Nevertheless, indirect methods have been also developed with the aim of taking a step further towards improving its quantitative determination. Mainly, these indirect methods are based on the addition of a probe which after reacting with $^1\text{O}_2$ 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.

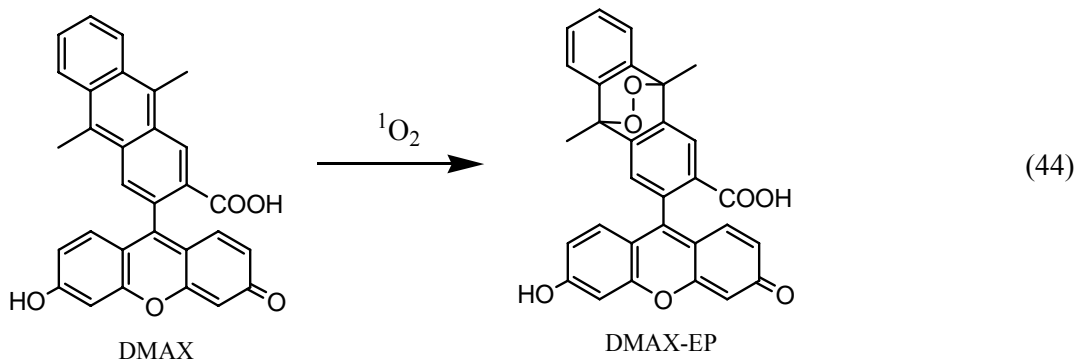
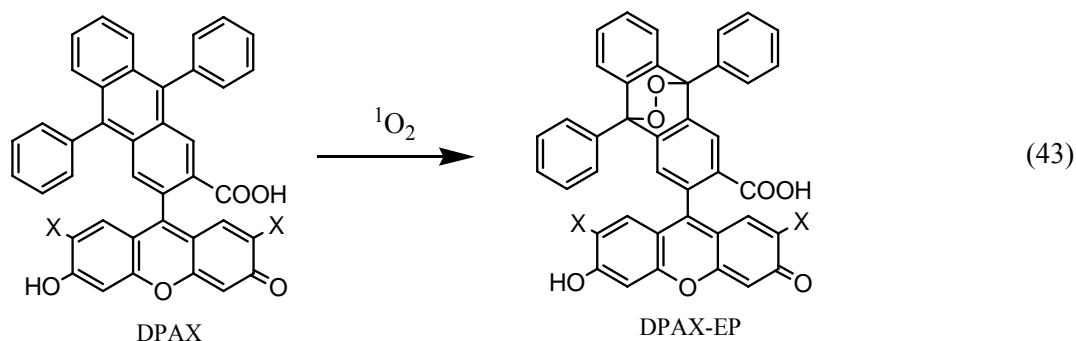
One of the probes used in the determination of $^1\text{O}_2$ is the Singlet Oxygen Sensor Green reagent (SOSG) that reacts with $^1\text{O}_2$ leading to the formation of a highly fluorescent endoperoxide (SOSG-EP) (reaction (41)), which is then measured by spectrofluorometry. Its feasibility for the quantitative measurement of $^1\text{O}_2$ 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 $^1\text{O}_2$ 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 $^1\text{O}_2$ scavenging. The main

advantage of using SOSG and FFA as molecular probes, together with their good selectivity, is the commercial availability of these compounds.

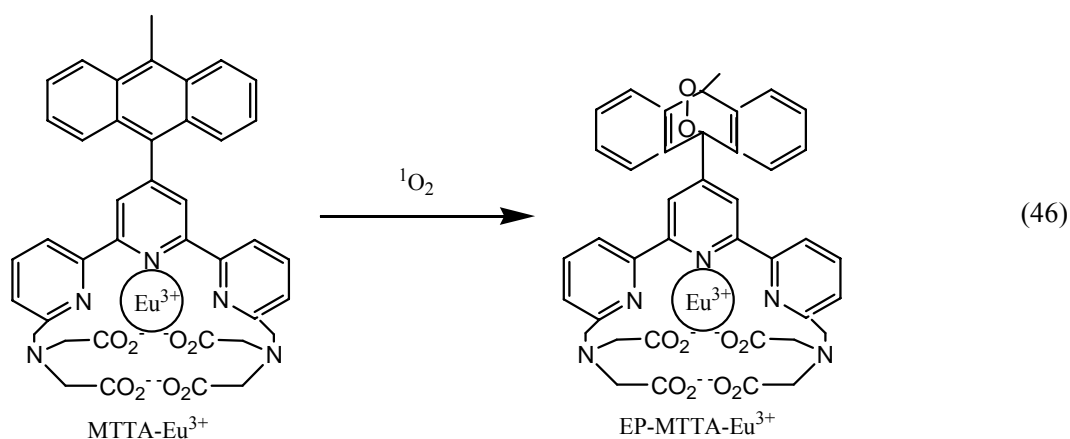
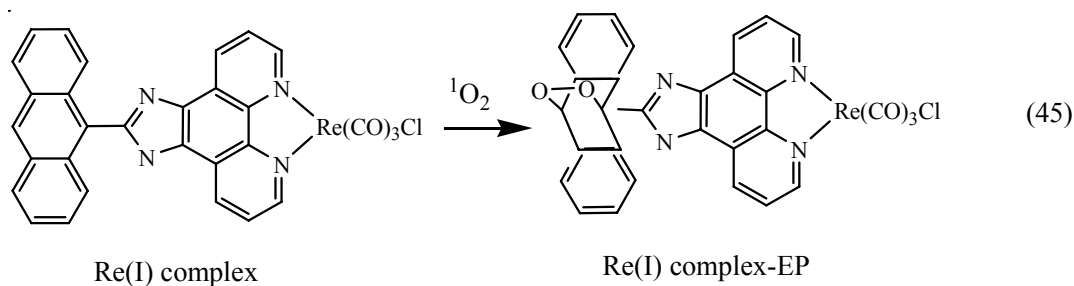


In contrast to SOSG or furfuryl alcohol, which are commercially available, most of the specific compounds used along the quantitative determination of $^1\text{O}_2$ have been synthesized in the laboratory. These compounds are based in relatively complex aromatic structure in which the reaction with $^1\text{O}_2$ 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 ($\text{MoO}_4^{2-}/\text{H}_2\text{O}_2$).¹⁶⁵ The fluorescent product after the reaction with $^1\text{O}_2$ 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 $^1\text{O}_2$.





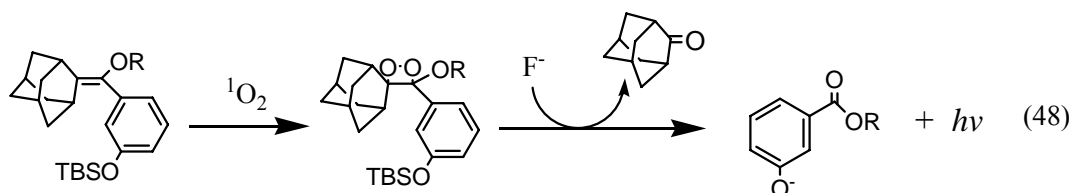
Another group that has also demonstrated high selectivity and good response towards $^1\text{O}_2$ comprises chelate-based luminescence probes. Rhenium complex, $\text{Re}(\text{CO})_3\text{Cl}(\text{aeip})$ [aeip: 2-(anthracen-9-yl)-1-ethyl-imidazo[4,5-f][1,10]phenanthroline],¹⁵³ europium complex, 4'-(10-methyl-9-anthryl)-2,2':6',2''-terpyridine-6,6''-diyl]bis(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 synthesized in laboratory and react with $^1\text{O}_2$ yielding luminescent endoperoxides (reactions (45)-(47)). The assessment of the influence of experimental parameters such as pH and the presence of other reactive species ($\bullet\text{OH}$, 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.



As
alte
rnat
ive
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 $^1\text{O}_2$ 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 ($\bullet\text{OH}$, $\text{O}_2^{\bullet-}$ and H_2O_2) present in solution were evaluated.



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 $\text{H}_2\text{O}_2/\text{NaOCl}$, evaluating the influence of different ROS such as $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$ 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 $^1\text{O}_2$ 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 $^1\text{O}_2$. 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 $^1\text{O}_2$.

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

This research was supported by the Ministry of Competitiveness and Education (MINECO/SPAIN) under the project CTQ2011-25262. Pablo Fernandez-Castro is grateful to MINECO for the FPI fellowship BES-2012-054790.

REFERENCES

1. Wang J, Guo Y, Liu B, Jin X, Liu L, Xu R, Kong Y, Wang B, Detection and analysis of reactive oxygen species (ROS) generated by nano-sized TiO₂ powder under ultrasonic irradiation and application in sonocatalytic degradation of organic dyes. *Ultrason Sonochem* **18** :177-83 (2011).
2. Kwon BG, Kwon J-H, Measurement of the hydroxyl radical formation from H₂O₂, NO₃⁻, and Fe(III) using a continuous flow injection analysis. *J Ind Eng Chem* **16** :193-9 (2010).
3. Wols BA, Hofman-Caris CHM, Review of photochemical reaction constants of organic micropollutants required for UV advanced oxidation processes in water. *Water Res* **46** :2815-27 (2012).

4. Yang X-J, Xu X-M, Xu J, Han Y-F, Iron oxychloride (FeOCl): An efficient fenton-like catalyst for producing hydroxyl radicals in degradation of organic contaminants. *J Am Chem Soc* **135** :16058-61 (2013).
5. He Y, Grieser F, Ashokkumar M, Kinetics and mechanism for the sonophotocatalytic degradation of p -chlorobenzoic acid. *J Phys Chem A* **115** :6582-8 (2011).
6. Czili H, Horváth A, Applicability of coumarin for detecting and measuring hydroxyl radicals generated by photoexcitation of TiO₂ nanoparticles. *Appl Catal B-Environ* **81** :295-302 (2008).
7. Anglada Á, Urriaga A, Ortiz I, Contributions of electrochemical oxidation to waste-water treatment: Fundamentals and review of applications. *J Chem Technol Biotechnol* **84** :1747-55 (2009).
8. Ikehata K, Jodeiri Naghashkar N, Gamal El-Din M, Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: A review. *Ozone- Sci Eng* **28** :353-414 (2006).
9. Feng L, van Hullebusch ED, Rodrigo MA, Esposito G, Oturan MA, Removal of residual anti-inflammatory and analgesic pharmaceuticals from aqueous systems by electrochemical advanced oxidation processes. A review. *Chem Eng J* **228** :944-64 (2013).
10. Urriaga A, Fernandez-Castro P, Gómez P, Ortiz I, Remediation of wastewaters containing tetrahydrofuran. study of the electrochemical mineralization on BDD electrodes. *Chem Eng J* **239** :341-50 (2014).
11. Konstantinou IK, Albanis TA, TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations: A review. *Appl Catal B- Environ* **49** :1-14 (2004).
12. Oller I, Malato S, Sánchez-Pérez JA, Combination of advanced oxidation processes and biological treatments for wastewater decontamination-A review. *Sci Total Environ* **409** :4141-66 (2011).
13. Cañizares P, Lobato J, Paz R, Rodrigo MA, Sáez C, Advanced oxidation processes for the treatment of olive-oil mills wastewater. *Chemosphere* **67** :832-8 (2007).
14. Zhou Q, Li W, Hua T, Removal of organic matter from landfill leachate by advanced oxidation processes: A review. *Int J Chem Eng* : article number 270532 (2010).

15. Rizzo L, Bioassays as a tool for evaluating advanced oxidation processes in water and wastewater treatment. *Water Res* **45** :4311-40 (2011).
16. Primo O, Rivero MJ, Ortiz I, Photo-fenton process as an efficient alternative to the treatment of landfill leachates. *J Hazard Mater* **153** :834-42 (2008).
17. Anglada Á, Urtiaga AM, Ortiz I, Laboratory and pilot plant scale study on the electrochemical oxidation of landfill leachate. *J Hazard Mater* **181** :729-35 (2010).
18. Pérez G, Saiz J, Ibañez R, Urtiaga AM, Ortiz I, Assessment of the formation of inorganic oxidation by-products during the electrocatalytic treatment of ammonium from landfill leachates. *Water Res* **46** :2579-90 (2012).
19. Antonopoulou M, Evgenidou E, Lambropoulou D, Konstantinou I, A review on advanced oxidation processes for the removal of taste and odor compounds from aqueous media. *Water Res* **53** :215-34 (2014).
20. Ribeiro AR, Nunes OC, Pereira MFR, Silva AMT, An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched directive 2013/39/EU. *Environ Int* **75** :33-51 (2015).
21. Vallejo M, Fresnedo San Román M, Ortiz I, Irabien A, Overview of the PCDD/Fs degradation potential and formation risk in the application of advanced oxidation processes (AOPs) to wastewater treatment. *Chemosphere* **118** :44-56 (2015).
22. Vallejo M, San Román MF, Irabien A, Ortiz I, Comparative study of the destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans during fenton and electrochemical oxidation of landfill leachates. *Chemosphere* **90** :132-8 (2013).
23. Tung C-H, Chang J-H, Hsieh Y-H, Hsu J-C, Ellis AV, Liu W-C, Yan R-H, Comparison of hydroxyl radical yields between photo- and electro-catalyzed water treatments. *J Taiwan Inst Chem E* (2014).

24. Gualandi I, Tonelli D, A new electrochemical sensor for OH radicals detection. *Talanta* **115** :779-86 (2013).
25. Bubacz K, Kusiak-Nejman E, Tryba B, Morawski AW, Investigation of OH radicals formation on the surface of TiO₂/N photocatalyst at the presence of terephthalic acid solution. estimation of optimal conditions. *J Photochem Photobiol A* **261** :7-11 (2013).
26. Hu Y-L, Lu Y, Zhou G-J, Xia X-H, A simple electrochemical method for the determination of hydroxyl free radicals without separation process. *Talanta* **74** :760-5 (2008).
27. Rivas FJ, Beltran FJ, Frades J, Buxeda P, Oxidation of p-hydroxybenzoic acid by fenton's reagent. *Water Res* **35** :387-96 (2001).
28. Burns JM, Cooper WJ, Ferry JL, King DW, DiMento BP, McNeill K, Miller CJ, Miller WL, Peake BM, Rusak SA, Rose AL, Waite TD, Methods for reactive oxygen species (ROS) detection in aqueous environments. *Aquat Sci* **74** :683-734 (2012).
29. Page SE, Arnold WA, McNeill K, Terephthalate as a probe for photochemically generated hydroxyl radical. *J Environ Monitor* **12** :1658-65 (2010).
30. Bartosz G, Use of spectroscopic probes for detection of reactive oxygen species, *Clin Chim Acta* **368** :53-76 (2006).
31. Gomes A, Fernandes E, Lima JLFC, Fluorescence probes used for detection of reactive oxygen species. *J Biochem Biophys Methods* **65** :45-80 (2005).
32. Buxton GV, Greenstock CL, Helman WP, Ross AB, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (\square OH/ \square O⁻ in aqueous solution. *J Phys Chem Ref Data* **17** :513-886 (1988).
33. Zhang B-T, Zhao L-X, Lin J-M, Study on superoxide and hydroxyl radicals generated in indirect electrochemical oxidation by chemiluminescence and UV-visible spectra. *J Environ Sci* **20** :1006-11 (2008).

34. Newton GL, Milligan JR, Fluorescence detection of hydroxyl radicals. *Radiat Phys Chem* **75** :473-8 (2006).
35. Nosaka Y, Nosaka AY, Identification and roles of the active species generated on various photocatalysts. Wiley-VCH Verlag GmbH & Co. KGaA, 1-24 (2013).
36. Soh N, Recent advances in fluorescent probes for the detection of reactive oxygen species. *Anal Bioanal Chem* **386** :532-43 (2006).
37. Lu C, Song G, Lin J-M, Reactive oxygen species and their chemiluminescence-detection methods. *TrAC - Trends Anal Chem* **25** :985-95 (2006).
38. Guinea E, Arias C, Cabot PL, Garrido JA, Rodríguez RM, Centellas F, Brillas E, Mineralization of salicylic acid in acidic aqueous medium by electrochemical advanced oxidation processes using platinum and boron-doped diamond as anode and cathodically generated hydrogen peroxide. *Water Res* **42** :499-511 (2008).
39. Yuan S, Chen M, Mao X, Alshawabkeh AN, A three-electrode column for pd-catalytic oxidation of TCE in groundwater with automatic pH-regulation and resistance to reduced sulfur compound foiling. *Water Res* **47** :269-78 (2013).
40. de Luna MDG, Colades JI, Su C-C, Lu M-C, Comparison of dimethyl sulfoxide degradation by different fenton processes. *Chem Eng J* **232** :418-24 (2013).
41. Tang Q, Jiang W, Cheng Y, Lin S, Lim TM, Xiong J, Generation of reactive species by gas-phase dielectric barrier discharges. *Ind Eng Chem Res* **50** :9839-46 (2011).
42. Sahni M, Locke BR, Quantification of hydroxyl radicals produced in aqueous phase pulsed electrical discharge reactors. *Ind Eng Chem Res* **45** :5819-25 (2006).
43. Tai C, Peng J-F, Liu J-F, Jiang G-B, Zou H, Determination of hydroxyl radicals in advanced oxidation processes with dimethyl sulfoxide trapping and liquid chromatography. *Anal Chim Acta* **527** :73-80 (2004).

44. Lee Y, Lee C, Yoon J, Kinetics and mechanisms of DMSO (dimethylsulfoxide) degradation by UV/H₂O₂ process. *Water Res* **38** :2579-88 (2004).
45. Tai C, Gu X, Zou H, Guo Q, A new simple and sensitive fluorometric method for the determination of hydroxyl radical and its application. *Talanta* **58** :661-7 (2002).
46. Yang X-F, Guo X-Q, Study of nitroxide-linked naphthalene as a fluorescence probe for hydroxyl radicals. *Anal Chim Acta* **434** :169-77 (2001).
47. Vaughan PP, Blough NV, Photochemical formation of hydroxyl radical by constituents of natural waters. *Environ Sci Technol* **32** :2947-53 (1998).
48. METHOD 8315A determination of carbonyl compounds by high performance liquid chromatography (HPLC), U.S. environmental protection agency. (1996).
49. Dominguez S, Ribao P, Rivero MJ, Ortiz I, Influence of radiation and TiO₂ concentration on the hydroxyl radicals generation in a photocatalytic LED reactor. application to dodecylbenzenesulfonate degradation. *Appl Catal B-Environ* (doi:10.1016/j.apcatb.2014.09.072).
50. Comninellis C, Chen G, Electrochemistry for the environment. Springer, (2010).
51. Diez L, Livertoux M-H, Stark A-A, Wellman-Rousseau M, Leroy P, High-performance liquid chromatographic assay of hydroxyl free radical using salicylic acid hydroxylation during in vitro experiments involving thiols. *J Chromatogr B* **763** :185-93 (2001).
52. Jen J-F, Leu M-F, Yang TC, Determination of hydroxyl radicals in an advanced oxidation process with salicylic acid trapping and liquid chromatography. *J Chromatogr A* **796** :283-8 (1998).
53. Li S, Hu S, Zhang H, Formation of hydroxyl radicals and hydrogen peroxide by a novel nanosecond pulsed plasma power in water. *IEEE Trans Plasma Sci* **40** :63-7 (2012).
54. Ai S, Wang Q, Li H, Jin L, Study on production of free hydroxyl radical and its reaction with salicylic acid at lead dioxide electrode. *J Electroanal Chem* **578** :223-9 (2005).

55. Milne L, Stewart I, Bremner DH, Comparison of hydroxyl radical formation in aqueous solutions at different ultrasound frequencies and powers using the salicylic acid dosimeter. *Ultrason Sonochem* **20** :984-9 (2013).
56. Martínez-Tarifa A, Arrojo S, Ávila-Marín AL, Pérez-Jiménez JA, Sáez V, Ruiz-Lorenzo ML, Salicylic acid dosimetry applied for the statistical determination of significant parameters in a sonochemical reactor. *Chem Eng J* **157** :420-6 (2010).
57. Shimizu N, Ogino C, Dadjour MF, Ninomiya K, Fujihira A, Sakiyama K, Sonocatalytic facilitation of hydroxyl radical generation in the presence of TiO₂. *Ultrason Sonochem* **15** :988-94 (2008).
58. Amin LP, Gogate PR, Burgess AE, Bremner DH, Optimization of a hydrodynamic cavitation reactor using salicylic acid dosimetry. *Chem Eng J* **156** :165-9 (2010).
59. Arrojo S, Nerín C, Benito Y, Application of salicylic acid dosimetry to evaluate hydrodynamic cavitation as an advanced oxidation process. *Ultrason Sonochem* **14** :343-9 (2007).
60. Rabaoui N, Allagui MS, Anodic oxidation of salicylic acid on BDD electrode: Variable effects and mechanisms of degradation. *J Hazard Mater* **243** :187-92 (2012).
61. Peralta E, Roa G, Hernandez-Servin JA, Romero R, Balderas P, Natividad R, Hydroxyl radicals quantification by UV spectrophotometry. *Electrochim Acta* **129** :137-41 (2014).
62. Chen XM, da Silva DR, Martínez-Huitle CA, Application of advanced oxidation processes for removing salicylic acid from synthetic wastewaters. *Chin Chem Let* **21** :101-4 (2010).
63. Goi A, Veressinina Y, Trapido M, Degradation of salicylic acid by fenton and modified fenton treatment. *Chem Eng J* **143** :1-9 (2008).
64. Adán C, Coronado JM, Bellod R, Soria J, Yamaoka H, Photochemical and photocatalytic degradation of salicylic acid with hydrogen peroxide over TiO₂/SiO₂ fibres. *Appl Catal A-Gen* **303** :199-206 (2006).

65. Wang Y, Calas-Blanchard C, Cortina-Puig M, Baohong L, Marty J-L, An electrochemical method for sensitive determination of antioxidant capacity. *Electroanal* **21** :1395-400 (2009).
66. Han S, Nam S, Kang J, OH radical monitoring technologies for AOP advanced oxidation process. *Water Sci Technol* **46** :7-12 (2002).
67. Nam S, Han S, Kang J, Choi H, Kinetics and mechanisms of the sonolytic destruction of non-volatile organic compounds: Investigation of the sonochemical reaction zone using several OH monitoring techniques. *Ultrason Sonochem* **10** :139-47 (2003).
68. Chen C-, Jafvert CT, Photoreactivity of carboxylated single-walled carbon nanotubes in sunlight: Reactive oxygen species production in water. *Environ Sci Technol* **44** :6674-9 (2010).
69. Lan B, Huang R, Li L, Yan H, Liao G, Wang X, Zhang Q, Catalytic ozonation of p-chlorobenzoic acid in aqueous solution using Fe-MCM-41 as catalyst. *Chem Eng J* **219** :346-54 (2013).
70. Lester Y, Sharpless CM, Mamane H, Linden KG, Production of photo-oxidants by dissolved organic matter during UV water treatment. *Environ Sci Technol* **47** :11726-33 (2013).
71. Zhou X, Mopper K, Determination of photochemically produced hydroxyl radicals in seawater and freshwater. *Mar Chem* **30** :71-88 (1990).
72. Oturan MA, Pinson J, Hydroxylation by electrochemically generated OH• radicals. mono- and polyhydroxylation of benzoic acid: Products and isomers' distribution. *J Phys Chem* **99** :13948-54 (1995).
73. Lindsey ME, Tarr MA, Quantitation of hydroxyl radical during fenton oxidation following a single addition of iron and peroxide. *Chemosphere* **41** :409-17 (2000).
74. Ciotti C, Baciocchi R, Tuhkanen T, Influence of the operating conditions on highly oxidative radicals generation in fenton's systems. *J Hazard Mater* **161** :402-8 (2009).
75. Gazi S, Ananthkrishnan R, Semi-quantitative determination of hydroxyl radicals by benzoic acid hydroxylation: An analytical methodology for photo-fenton systems. *Curr Anal Chem* **8** :143-9 (2012).

76. Zhao J, Yang J, Ma J, Mn(II)-enhanced oxidation of benzoic acid by fe(III)/H₂O₂ system. *Chem Eng J* **239** :171-7 (2014).
77. Zhang C, Wang L, Wu F, Deng N, Quantitation of hydroxyl radicals from photolysis of fe(III)-citrate complexes in aerobic water. *Environ Sci Pollut R* **13** :156-60 (2006).
78. Wang L, Zhang C, Wu F, Deng N, Glebov EM, Bazhin NM, Determination of hydroxyl radicals from photolysis of fe(III)-pyruvate complexes in homogeneous aqueous solution. *React Kinet Catal L* **89** :183-92 (2006).
79. Nakatani N, Hashimoto N, Shindo H, Yamamoto M, Kikkawa M, Sakugawa H, Determination of photoformation rates and scavenging rate constants of hydroxyl radicals in natural waters using an automatic light irradiation and injection system. *Anal Chim Acta* **581** :260-7 (2007).
80. Wu F, Li J, Peng Z, Deng N, Photochemical formation of hydroxyl radicals catalyzed by montmorillonite. *Chemosphere* **72** :407-13 (2008).
81. Oliveira RTS, Salazar-Banda GR, Santos MC, Calegari ML, Miwa DW, Machado SAS, Avaca LA, Electrochemical oxidation of benzene on boron-doped diamond electrodes. *Chemosphere* **66** :2152-8 (2007).
82. Fang YF, Deng AP, Huang YP, Determination of hydroxyl radical in fenton system. *Chin Chem Let* **20** :1235-40 (2009).
83. Westerhoff P, Mezyk SP, Cooper WJ, Minakata D, Electron pulse radiolysis determination of hydroxyl radical rate constants with suwannee river fulvic acid and other dissolved organic matter isolates. *Environ Sci Technol* **41** :4640-6 (2007).
84. Kim JK, Metcalfe IS, Investigation of the generation of hydroxyl radicals and their oxidative role in the presence of heterogeneous copper catalysts. *Chemosphere* **69** :689-96 (2007).
85. Du Y, Fu QS, Li Y, Su Y, Photodecomposition of 4-chlorophenol by reactive oxygen species in UV/air system. *J Hazard Mater* **186** :491-6 (2011).

86. Yang J, Dai J, Chen C, Zhao J, Effects of hydroxyl radicals and oxygen species on the 4-chlorophenol degradation by photoelectrocatalytic reactions with TiO₂-film electrodes. *J Photochem Photobiol A* **208** :66-77 (2010).
87. Cermenati L, Pichat P, Guillard C, Albini A, Probing the TiO₂ photocatalytic mechanisms in water purification by use of quinoline, photo-fenton generated OH. radicals and superoxide dismutase. *J Phys Chem B* **101** :2650-8 (1997).
88. Jing J, Li W, Boyd A, Zhang Y, Colvin VL, Yu WW, Photocatalytic degradation of quinoline in aqueous TiO₂ suspension. *J Hazard Mater* **237-238** :247-55 (2012).
89. Muff J, Bennedsen LR, Søgaaard EG, Study of electrochemical bleaching of p-nitrosodimethylaniline and its role as hydroxyl radical probe compound. *J Appl Electrochem* **41** :599-607 (2011).
90. Kim C, Park H-, Cha S, Yoon J, Facile detection of photogenerated reactive oxygen species in TiO₂ nanoparticles suspension using colorimetric probe-assisted spectrometric method. *Chemosphere* **93** :2011-5 (2013).
91. Simonsen ME, Muff J, Bennedsen LR, Kowalski KP, Søgaaard EG, Photocatalytic bleaching of p-nitrosodimethylaniline and a comparison to the performance of other AOP technologies. *J Photochem Photobiol A* **216** :244-9 (2010).
92. Guo Y, Cheng C, Wang J, Wang Z, Jin X, Li K, Kang P, Gao J, Detection of reactive oxygen species (ROS) generated by TiO₂(R), TiO₂(R/A) and TiO₂(A) under ultrasonic and solar light irradiation and application in degradation of organic dyes. *J Hazard Mater* **192** :786-93 (2011).
93. Yu F, Xu D, Lei R, Li N, Li K, Free-radical scavenging capacity using the fenton reaction with rhodamine B as the spectrophotometric indicator. *J Agric Food Chem* **56** :730-5 (2008).
94. Li M, Carlson S, Kinzer JA, Perpall HJ, HPLC and LC-MS studies of hydroxylation of phenylalanine as an assay for hydroxyl radicals generated from udenfriend's reagent. *Biochem Biophys Res Commun* **312** :316-22 (2003).

95. Mencigar DP, Strlic M, Štangar UL, Korošec RC, Hydroxyl radical scavenging-based method for evaluation of TiO₂ photocatalytic activity. *Acta Chim Slov* **60** :908-12 (2013).
96. Charbouillot T, Brigante M, Mailhot G, Maddigapu PR, Minero C, Vione D, Performance and selectivity of the terephthalic acid probe for •OH as a function of temperature, pH and composition of atmospherically relevant aqueous media. *J Photochem Photobiol A* **222** :70-6 (2011).
97. Ishibashi K-I, Fujishima A, Watanabe T, Hashimoto K, Quantum yields of active oxidative species formed on TiO₂ photocatalyst. *J Photochem Photobiol A* **134** :139-42 (2000).
98. Villeneuve L, Alberti L, Steghens J-P, Lancelin J-M, Mestas J-L, Assay of hydroxyl radicals generated by focused ultrasound. *Ultrason Sonochem* **16** :339-44 (2009).
99. Linxiang L, Abe Y, Nagasawa Y, Kudo R, Usui N, Imai K, Mashino T, Mochizuki M, Miyata N, An HPLC assay of hydroxyl radicals by the hydroxylation reaction of terephthalic acid. *Biomed Chromatogr* **18** :470-4 (2004).
100. Hirakawa T, Yawata K, Nosaka Y, Photocatalytic reactivity for O₂{radical dot}- and OH{radical dot} radical formation in anatase and rutile TiO₂ suspension as the effect of H₂O₂ addition. *Appl Catal A-Gen* **325** :105-11 (2007).
101. Hirakawa T, Nosaka Y, Properties of O₂ .- and OH. formed in TiO₂ aqueous suspensions by photocatalytic reaction and the influence of H₂O₂ and some ions. *Langmuir* **18** :3247-54 (2002).
102. Ishibashi K-I, Fujishima A, Watanabe T, Hashimoto K, Detection of active oxidative species in TiO₂ photocatalysis using the fluorescence technique. *Electrochem Commun* **2** :207-10 (2000).
103. Nakabayashi Y, Nosaka Y, OH radical formation at distinct faces of rutile TiO₂ crystal in the procedure of photoelectrochemical water oxidation. *J Phys Chem C* **117** :23832-9 (2013).
104. Ikhlaq A, Brown DR, Kasprzyk-Hordern B, Mechanisms of catalytic ozonation on alumina and zeolites in water: Formation of hydroxyl radicals. *Appl Catal B-Environ* **123-124** :94-106 (2012).

105. Zhang J, Nosaka Y, Quantitative detection of OH radicals for investigating the reaction mechanism of various visible-light TiO₂ photocatalysts in aqueous suspension. *J Phys Chem C* **117** :1383-91 (2013).
106. Cernigoj U, Štangar UL, Trebše P, Sarakha M, Determination of catalytic properties of TiO₂ coatings using aqueous solution of coumarin: Standardization efforts. *J Photochem Photobiol A* **201** :142-50 (2009).
107. Oguma J, Kakuma Y, Murayama S, Nosaka Y, Effects of silica coating on photocatalytic reactions of anatase titanium dioxide studied by quantitative detection of reactive oxygen species. *Appl Catal B-Environ* **129** :282-6 (2013).
108. Bejan D, Guinea E, Bunce NJ, On the nature of the hydroxyl radicals produced at boron-doped diamond and ebonex ® anodes. *Electrochim Acta* **69** :275-81 (2012).
109. Maezono T, Tokumura M, Sekine M, Kawase Y, Hydroxyl radical concentration profile in photo-fenton oxidation process: Generation and consumption of hydroxyl radicals during the discoloration of azo-dye orange II. *Chemosphere* **82** :1422-30 (2011).
110. Guan H, Zhu L, Zhou H, Tang H, Rapid probing of photocatalytic activity on titania-based self-cleaning materials using 7-hydroxycoumarin fluorescent probe. *Anal Chim Acta* **608** :73-8 (2008).
111. Louit G, Foley S, Cabillic J, Coffigny H, Taran F, Valleix A, Renault JP, Pin S, The reaction of coumarin with the OH radical revisited: Hydroxylation product analysis determined by fluorescence and chromatography. *Radiat Phys Chem* **72** :119-24 (2005).
112. Baldacchino G, Maeyama T, Yamashita S, Taguchi M, Kimura A, Katsumura Y, Murakami T, Determination of the time-dependent OH-yield by using a fluorescent probe. application to heavy ion irradiation. *Chem Phys Lett* **468** :275-9 (2009).
113. Manevich Y, Held KD, Biaglow JE, Coumarin-3-carboxylic acid as a detector for hydroxyl radicals generated chemically and by gamma radiation. *Radiat Res* **148** :580-91 (1997).

114. Jing JG, Ke HX, Ji XH, Huang H, Tang B, Determination of trace hydroxyl radicals by flow injection spectrofluorometry and its analytical application. *J Agric Food Chem* **54** :7968-72 (2006).
115. Tang B, Zhang L, Geng Y, Determination of the antioxidant capacity of different food natural products with a new developed flow injection spectrofluorimetry detecting hydroxyl radicals. *Talanta* **65** :769-75 (2005).
116. Shafaei A, Nikazar M, Arami M, Photocatalytic degradation of terephthalic acid using titania and zinc oxide photocatalysts: Comparative study. *Desalination* **252** :8-16 (2010).
117. Backa S, Jansbo K, Reitberger T, Detection of hydroxyl radicals by a chemiluminescence method - A critical review. *Holzforschung* **51** :557-64 (1997).
118. Miller CJ, Rose AL, Waite TD, Hydroxyl radical production by H₂O₂-mediated oxidation of Fe(II) complexed by suwannee river fulvic acid under circumneutral freshwater conditions. *Environ Sci Technol* **47** :829-35 (2013).
119. Miller CJ, Rose AL, Waite TD, Phthalhydrazide chemiluminescence method for determination of hydroxyl radical production: Modifications and adaptations for use in natural systems. *Anal Chem* **83** :261-8 (2011).
120. Nobushi Y, Uchikura K, Selective detection of hydroxyl radical scavenging capacity based on electrogenerated chemiluminescence detection using tris(2,2'-bipyridine) ruthenium(III) by flow injection analysis. *Chem Pharm Bull* **58** :117-20 (2010).
121. Tsai C-H, Stern A, Chiou J-F, Chern C-L, Liu T-Z, Rapid and specific detection of hydroxyl radical using an ultraweak chemiluminescence analyzer and a low-level chemiluminescence emitter: Application to hydroxyl radical-scavenging ability of aqueous extracts of food constituents. *J Agric Food Chem* **49** :2137-41 (2001).
122. Grela MA, Coronel MEJ, Colussi AJ, Quantitative spin-trapping studies of weakly illuminated titanium dioxide sols. implications for the mechanism of photocatalysis. *J Phys Chem* **100** :16940-6 (1996).

123. Yanagida H, Masubuchi Y, Minagawa K, Ogata T, Takimoto J-I, Koyama K, A reaction kinetics model of water sonolysis in the presence of a spin-trap. *Ultrason Sonochem* **5** :133-9 (1999).
124. Han SK, Hwang T-M, Yoon Y, Kang J-W, Evidence of singlet oxygen and hydroxyl radical formation in aqueous goethite suspension using spin-trapping electron paramagnetic resonance (EPR). *Chemosphere* **84** :1095-101 (2011).
125. Cong Y, Wu Z, Electrocatalytic generation of radical intermediates over lead dioxide electrode doped with fluoride. *J Phys Chem C* **111** :3442-6 (2007).
126. Marselli B, Garcia-Gomez J, Michaud P-A, Rodrigo MA, Comninellis C, Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes. *J Electrochem Soc* **150** :D79-83 (2003).
127. Li L, Abe Y, Kanagawa K, Usui N, Imai K, Mashino T, Mochizuki M, Miyata N, Distinguishing the 5,5-dimethyl-1-pyrroline N-oxide (DMPO)-OH radical quenching effect from the hydroxyl radical scavenging effect in the ESR spin-trapping method. *Anal Chim Acta* **512** :121-4 (2004).
128. Granados-Oliveros G, Gómez-Vidales V, Nieto-Camacho A, Morales-Serna JA, Cárdenas J, Salmón M, Photoproduction of H₂O₂ and hydroxyl radicals catalysed by natural and super acid-modified montmorillonite and its oxidative role in the peroxidation of lipids. *RSC Advances* **3** :937-44 (2013).
129. Kochany J, Bolton JR, Mechanism of photodegradation of aqueous organic pollutants. 2. measurement of the primary rate constants for reaction of OH radicals with benzene and some halobenzenes using an EPR spin-trapping method following the photolysis of H₂O₂. *Environ Sci Technol* **26** :262-5 (1992).
130. Yang F, Zhang R, He J, Abliz Z, Development of a liquid chromatography/electrospray ionization tandem mass spectrometric method for the determination of hydroxyl radical. *Rapid Commun Mass Spectrom* **21** :107-11 (2007).
131. Khramtsov VV, Reznikov VA, Berliner LJ, Litkin AK, Grigor'ev IA, Clanton TL, NMR spin trapping: Detection of free radical reactions with a new fluorinated DMPO analog. *Free Radical Biol Med* **30** :1099-107 (2001).

132. Schwarz PF, Turro NJ, Bossmann SH, Braun AM, Abdel Wahab A-A, Dürr H, A new method to determine the generation of hydroxyl radicals in illuminated TiO₂ suspensions. *J Phys Chem B* **101** :7127-34 (1997).
133. Rosen GM, Tsai P, Barth ED, Dorey G, Casara P, Spedding M, Halpern HJ, A one-step synthesis of 2-(2-pyridyl)-3H-indol-3-one N-oxide: Is it an efficient spin trap for hydroxyl radical? *J Org Chem* **65** :4460-3 (2000).
134. Mahé E, Bornoz P, Briot E, Chevalet J, Comminellis C, Devilliers D, A selective chemiluminescence detection method for reactive oxygen species involved in oxygen reduction reaction on electrocatalytic materials. *Electrochim Acta* **102** :259-73 (2013).
135. Wang Q, Ding F, Zhu N, Li H, He P, Fang Y, Determination of hydroxyl radical by capillary zone electrophoresis with amperometric detection. *J Chromatogr A* **1016** :123-8 (2003).
136. Cao Y, Chu Q, Ye J, Determination of hydroxyl radical by capillary electrophoresis and studies on hydroxyl radical scavenging activities of chinese herbs. *Anal Bioanal Chem* **376** :691-5 (2003).
137. Kilinc E, Determination of the hydroxyl radical by its adduct formation with phenol and liquid chromatography/electrochemical detection. *Talanta* **65** :876-81 (2005).
138. Chatzisyneon E, Fierro S, Karafyllis I, Mantzavinos D, Kalogerakis N, Katsaounis A, Anodic oxidation of phenol on Ti/IrO₂ electrode: Experimental studies. *Catal Today* **151** :185-9 (2010).
139. Bielski BH, Cabelli DE, Arudi RL, Ross AB, Reactivity of HO₂/O⁻² radicals in aqueous solution. *J Phys Chem Ref Data* **14** :1041-100 (1985).
140. Sawyer DT, Valentine JS, How super is superoxide? *Acc Chem Res* **14** :393-400 (1981).
141. Heller MI, Croot PL, Application of a superoxide (O₂⁻) thermal source (SOTS-1) for the determination and calibration of O₂⁻ fluxes in seawater. *Anal Chim Acta* **667** :1-13 (2010).
142. Rose AL, Waite TD, Chemiluminescence of luminol in the presence of iron(II) and oxygen: Oxidation mechanism and implications for its analytical use. *Anal Chem* **73** :5909-20 (2001).

143. Nosaka Y, Takahashi S, Sakamoto H, Nosaka AY, Reaction mechanism of cu(II)-grafted visible-light responsive TiO₂ and WO₃ photocatalysts studied by means of ESR spectroscopy and chemiluminescence photometry. *J Phys Chem C* **115** :21283-90 (2011).
144. Hirakawa T, Nosaka Y, Selective production of superoxide ions and hydrogen peroxide over nitrogen- and sulfur-doped TiO₂ photocatalysts with visible light in aqueous suspension systems. *J Phys Chem C* **112** :15818-23 (2008).
145. Wu X-, Lingyue M, Akiyama K, Chemiluminescence study of active oxygen species produced by TiO₂ photocatalytic reaction. *Luminescence* **20** :36-40 (2005).
146. Hirakawa T, Kominami H, Ohtani B, Nosaka Y, Mechanism of photocatalytic production of active oxygens on highly crystalline TiO₂ particles by means of chemiluminescent probing and ESR spectroscopy. *J Phys Chem B* **105** :6993-9 (2001).
147. Nosaka Y, Yamashita Y, Fukuyama H, Application of chemiluminescent probe to monitoring superoxide radicals and hydrogen peroxide in TiO₂ photocatalysis. *J Phys Chem B* **101** :5822-7 (1997).
148. Xu X, Duan X, Yi Z, Zhou Z, Fan X, Wang Y, Photocatalytic production of superoxide ion in the aqueous suspensions of two kinds of ZnO under simulated solar light. *Catal Commun* **12** :169-72 (2010).
149. Goto H, Hanada Y, Ohno T, Matsumura M, Quantitative analysis of superoxide ion and hydrogen peroxide produced from molecular oxygen on photoirradiated TiO₂ particles. *J Catal* **225** :223-9 (2004).
150. Kwon BG, Kim J-O, Kwon J-K, An advanced kinetic method for HO₂•/O₂•⁻ determination by using terephthalate in the aqueous solution. *Environ Eng Res* **17** :205-10 (2012).
151. Kwon BG, Characterization of the hydroperoxyl/superoxide anion radical (HO₂{radical dot}/O₂{radical dot}-) formed from the photolysis of immobilized TiO₂ in a continuous flow. *J Photochem Photobiol A* **199** :112-8 (2008).

152. Kwon BG, Lee JH, A kinetic method for HO₂ /O₂ .- determination in advanced oxidation processes. *Anal Chem* **76** :6359-64 (2004).
153. Liu Y-J, Wang K-Z, Visible-light-excited singlet-oxygen luminescence probe based on re(CO)₃Cl(aeip). *Eur J Inorg Chem* :5214-9 (2008).
154. Adam W, Kazakov DV, Kazakov VP, Singlet-oxygen chemiluminescence in peroxide reactions. *Chem Rev* **105** :3371-87 (2005).
155. Wu H, Song Q, Ran G, Lu X, Xu B, Recent developments in the detection of singlet oxygen with molecular spectroscopic methods. *TrAC - Trends Anal Chem* **30** :133-41 (2011).
156. DeRosa MC, Crutchley RJ, Photosensitized singlet oxygen and its applications. *Coord Chem Rev* **233-234** :351-71 (2002).
157. Kearns DR, Physical and chemical properties of singlet molecular oxygen. *Chem Rev* **71** :395-427 (1971).
158. Schweitzer C, Schmidt R, Physical mechanisms of generation and deactivation of singlet oxygen. *Chem Rev* **103** :1685-757 (2003).
159. Baier J, Fuß T, Pöllmann C, Wiesmann C, Pindl K, Engl R, Baumer D, Maier M, Landthaler M, Bäumler W, Theoretical and experimental analysis of the luminescence signal of singlet oxygen for different photosensitizers. *J Photochem Photobiol B* **87** :163-73 (2007).
160. Daimon T, Nosaka Y, Formation and behavior of singlet molecular oxygen in TiO₂ photocatalysis studied by detection of near-infrared phosphorescence. *J Phys Chem C* **111** :4420-4 (2007).
161. Daimon T, Hirakawa T, Nosaka Y, Monitoring the formation and decay of singlet molecular oxygen in TiO₂ photocatalytic systems and the reaction with organic molecules. *Electrochem* **76** :136-9 (2008).

162. Daimon T, Hirakawa T, Kitazawa M, Suetake J, Nosaka Y, Formation of singlet molecular oxygen associated with the formation of superoxide radicals in aqueous suspensions of TiO₂ photocatalysts. *Appl Catal A-Gen* **340** :169-75 (2008).
163. Lin H, Shen Y, Chen D, Lin L, Wilson BC, Li B, Xie S, Feasibility study on quantitative measurements of singlet oxygen generation using singlet oxygen sensor green. *J Fluoresc* **23** :41-7 (2013).
164. Haag WR, Holgne J, Singlet oxygen in surface waters. 3. photochemical formation and steady-state concentrations in various types of waters. *Environ Sci Technol* **20** :341-8 (1986).
165. You MX, Wang YX, Wang H, Yang RH, Fluorescent detection of singlet oxygen: Amplifying signal transduction and improving sensitivity based on intramolecular FRET of anthryl appended porphyrins. *Chin Sci Bull* **56** :3253-9 (2011).
166. Umezawa N, Tanaka K, Urano Y, Kikuchi K, Higuchi T, Nagano T, Novel fluorescent probes for singlet oxygen. *Ange Chem Int Edit* **38** :2899-901 (1999).
167. Tanaka K, Miura T, Umezawa N, Urano Y, Kikuchi K, Higuchi T, Nagano T, Rational design of fluorescein-based fluorescence probes. mechanism-based design of a maximum fluorescence probe for singlet oxygen. *J Am Chem Soc* **123** :2530-6 (2001).
168. Song B, Wang G, Tan M, Yuan J, A europium(III) complex as an efficient singlet oxygen luminescence probe. *J Am Chem Soc* **128** :13442-50 (2006).
169. Tan M, Song B, Wang G, Yuan J, A new terbium(III) chelate as an efficient singlet oxygen fluorescence probe. *Free Radical Biol Med* **40** :1644-53 (2006).
170. Ruiz-González R, Zanooco R, Gidi Y, Zanooco AL, Nonell S, Lemp E, Naphthoxazole-based singlet oxygen fluorescent probes. *Photochem Photobiol* **89** :1427-32 (2013).
171. MacManus-Spencer LA, Latch DE, Kroncke KM, McNeill K, Stable dioxetane precursors as selective trap-and-trigger chemiluminescent probes for singlet oxygen. *Anal Chem* **77** :1200-5 (2005).

172. Li X, Zhang G, Ma H, Zhang D, Li J, Zhu D, 4,5-dimethylthio-4'-[2-(9-anthryloxy)ethylthio]tetrathiafulvalene, a highly selective and sensitive chemiluminescence probe for singlet oxygen. *J Am Chem Soc* **126** :11543-8 (2004).
173. Zheng X, Sun S, Zhang D, Ma H, Zhu D, A new chemiluminescence probe for singlet oxygen based on tetrathiafulvalene-anthracene dyad capable of performing detection in water/alcohol solution. *Anal Chim Acta* **575** :62-7 (2006).
174. Coolen SAJ, Huf FA, Reijenga JC, Determination of free radical reaction products and metabolites of salicylic acid using capillary electrophoresis and micellar electrokinetic chromatography. *J Chromatogr B* **717** :119-24 (1998).
175. Ishibashi K-I, Fujishima A, Watanabe T, Hashimoto K. Generation and deactivation processes of superoxide formed on TiO₂ film illuminated by very weak UV light in air or water. *J Phys Chem B* **104** :4934-8 (2000).

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, fluorescence 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 ₂ O 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 ($k_{\bullet\text{OH,pHBA}} = 6 \cdot 10^9$ l/mol/s > $k_{\bullet\text{OH,BA}} = 4.3 \cdot 10^9$ 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	Analysis of 7HC	Good selectivity towards •OH, though it may react with O ₃ Sensitive and fast method Good reproducibility	Disappearance of 7HC in the presence of O ₂ y O ₂ ^{•-} 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}	6, 41, 103- 111
	Fenton	HPLC with fluorescence detection or fluorescence spectrophotometry	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	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	
	Electrochemical oxidation	[•OH]: 1.6 nM- 0.02 mM	The direct photoelectrolysis of coumarin did not occur ¹⁰³	Photo-Fenton and electro-oxidation: reaction between 7HC and •OH ¹⁰⁴	
	γ-radiolysis		Coumarin is not oxidized in active anodes, it requires the presence of •OH ¹⁰⁴		
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 ^{•-} , ¹ O 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 •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 ₂ O ₂ that implies an underestimation in the quantification of •OH ⁴⁴	39-44
	Fenton	Analysis of C ₁₃ H ₁₅ O ₂ N 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 (95°C 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 •CH ₃ Competition between the reaction of •OH with DMSO and nitrite in anaerobe media Competition between the reaction of •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 ₂ OH) The EPR spectra in the presence of O ₂ ^{•-} 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 ^{•-} or H ₂ O 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 ₂ O 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 ^{•-} 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
Nitron: 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 Nitron does not react with O ₂ ^{•-}	The probe was synthesized in the laboratory The efficiency of the method is limited: the utility of nitron in the characterization of •OH is oriented to specific experimental designs Direct oxidation reaction with H ₂ O ₂	133
NPG: 0.5 mM	Photocatalysis	Analysis of 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 ₂ O 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 ₂ CO ₃ and organics act as scavengers of •OH H ₂ O 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 ' ⁻ , 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 ₂ O 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]: 4.17·10 ⁻¹³ M	RNO does not react with ¹ O ₂ , O ₂ ^{•-} 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]: 9.1·10 ⁻¹² -9.5·10 ⁻¹¹ M	Results consistent with those obtained with SA as a probe by HPLC analysis ROO• and O ₂ ^{•-} 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	2,3-dHBA and 2,5-dHBA	Selectivity SA-•OH Sensitivity, reproducibility and repeatability Stability of the products	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	24, 38, 51-64, 126, 135, 136, 174
	Photocatalysis Sonocatalysis Hydrodynamic cavitation Electrochemical technologies	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	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	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	
SCN ⁻ : 100 µM	Radiolysis	Analysis of (SCN) ₂ ^{•-} [•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	Analysis of OHTA	High sensitivity Rapid and simple technique One quantitative product	The reaction TA-•OH is affected by the solution pH Reaction of TA with O ₂ ^{•-} and H ₂ O ₂ The presence of inorganic salts and organics result in •OH scavenging	25, 29, 42, 65, 96- 102, 115, 116
	Photocatalysis Sonolysis Electrochemical methods	HPLC-UV/vis (pH 3), HPLC-fluorescence (pH 2.8 or 4.37), fluorescence spectrophotometry (pH 6- 11) [•OH]: 0.31-30 µM	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	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	

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

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
BA: 1 mM	Fenton system	Analysis of OHBA Fluorimetry (pH 11) [$O_2^{\cdot-}$]: 1 nM-3.1 μ M	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 μ M	Thermal decomposition	Analysis of the absorbance at a wavelength of 550 nm UV spectrophotometry [$O_2^{\cdot-}$]: 9 μ M	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 $O_2^{\cdot-}$	141
Luminol: 40 μ M- 7 mM	Fenton Photocatalysis Cyclic voltammetry	Analysis of the chemiluminescence generated Photon counting system with photomultiplier tube (pH 9-11) [$O_2^{\cdot-}$]: $3.9 \cdot 10^{-15}$ - $1.8 \cdot 10^{-4}$ 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, $N_3^{\cdot-}$, $CO_3^{\cdot-}$, $SCN^{\cdot-}$, $I^{\cdot-}$, $Br^{\cdot-}$, $Br_2^{\cdot-}$ 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 μ M	Photocatalysis Cyclic voltammetry Thermal decomposition	Analysis of the chemiluminescence generated Photon counting system with photomultiplier tube [$O_2^{\cdot-}$]: 25-60 nM	Selective towards $O_2^{\cdot-}/HO_2^{\cdot}$ and 1O_2 . $\cdot OH$ and H_2O_2 do not interfere in the analysis High sensitivity The method allows the quantification of $O_2^{\cdot-}/HO_2^{\cdot}$ at any pH	$O_2^{\cdot-}$ may react with buffer solutions containing amines Background chemiluminescence owing to the auto-oxidation of MCLA When $pH < pK_a = 7.75$, 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 ^{•-}]: Up to 5 μM	TA is more sensitive than BA	The half-life of O ₂ ^{•-} /HO ₂ [•] 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 ^{•-}]: 20 μM	-	NBD-Cl may react with amino acids, amines, thiols, ketyl and alkoxy radicals	141
NBT: 0.2-1 mM	Photocatalysis	Analysis of the absorbance of NBT or NBT-formazan UV-vis spectrophotometry [O ₂ ^{•-}]: Up to 0.17 mM	NBT does not react with •OH or H ₂ O ₂ NBT does not react with TiO ₂	Negligible formation of O ₂ ^{•-} /HO ₂ [•] under a N ₂ atmosphere 2-propanol scavenges O ₂ ^{•-} 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 ^{•-}]: 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 $^1\text{O}_2$

Probe	AOPs	Analytical features	Strengths	Limitations	Ref.
AAPD: 0.5-5 μM	Fenton-like	Analysis of the generated fluorescence Fluorescence spectrophotometry [$^1\text{O}_2$]: Qualitative	Selectivity towards $^1\text{O}_2$ High sensitivity	The probe is synthesized in the laboratory	165
Direct analysis	Photocatalysis	Monitoring of $^1\text{O}_2$ phosphorescence Photon-counting system with photomultiplier [$^1\text{O}_2$]: Up to 4.7 μM	Direct measurement	Under N_2 environments, the concentration of $^1\text{O}_2$ decreases, highlighting the importance of O_2 in its generation Methionine and folic acid act as $^1\text{O}_2$ scavengers The reaction with $\text{O}_2^{\cdot-}$ may deactivate $^1\text{O}_2$	160-162
DMAX: 10 μM	Thermal decomposition	Analysis of the fluorescence: formation of a fluorescent product Fluorescence spectrophotometry (pH 7.4) [$^1\text{O}_2$]: Qualitative	The reaction rate between $^1\text{O}_2$ 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 [$^1\text{O}_2$]: Qualitative	Good selectivity towards $^1\text{O}_2$ 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) [$^1\text{O}_2$]: $6.7 \cdot 10^{-14}$ - $1.8 \cdot 10^{-4}$ M	Good selectivity towards $^1\text{O}_2$ The reaction with $\text{O}_2^{\cdot-}$ 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 $^1\text{O}_2$ N_3^- quenches $^1\text{O}_2$	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 [¹ O ₂]: Qualitative	Good selectivity and sensitivity towards ¹ O 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 [¹ O ₂]: Study of the probe viability	Good selectivity towards ¹ O 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) [¹ O ₂]: 6.8 μM	Good selectivity and sensitivity towards ¹ O 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 [¹ O ₂]: Up to 40 mM	High selectivity and sensitivity towards ¹ O 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	2,3-dHBA and 2,5-dHBA	Selectivity SA-•OH Sensitivity, reproducibility and repeatability Stability of the products	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	24, 38, 51-64, 126, 135, 136, 174
	Photocatalysis Sonocatalysis Hydrodynamic cavitation Electrochemical technologies	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	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	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	
SCN ⁻ : 100 µM	Radiolysis	Analysis of (SCN) ₂ ^{*-} [•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	Analysis of OHTA	High sensitivity Rapid and simple technique One quantitative product	The reaction TA-•OH is affected by the solution pH Reaction of TA with O ₂ ^{*-} and H ₂ O ₂ The presence of inorganic salts and organics result in •OH scavenging An excess of NaTA may quench the fluorescence	25, 29, 42, 65, 96- 102, 115, 116
	Photocatalysis Sonolysis Electrochemical methods	HPLC-UV/vis (pH 3), HPLC-fluorescence (pH 2.8 or 4.37), fluorescence spectrophotometry (pH 6- 11) [•OH]: 0.31-30 µM	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	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	