



## Review

# Application of chemiluminescence in the analysis of wastewaters – A review



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## ABSTRACT

The toxicological effects of diverse pollutants typically found on wastewaters of diverse origin (industrial, urban, etc.) have led to regulation of their emission by national and trans-national organizations, and an increasing interest in the development of fast and reliable methods for their analysis.

This paper is an up-to-date comprehensive review on the analytical applications of chemiluminescence technique (characterized by high sensitivity, wide dynamic ranges and simple instrumentation) to the analysis of wastewaters, emphasizing the different kinds of pollutants that have been studied with these methods and discussing the different approaches followed by the authors as CL reactions, devices and coupled methods.

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## 1. Introduction

Many human activities as industrial processes or urban waste generation produce wastewaters containing pollutants of diverse nature. The introduction of these pollutants on the natural water systems and their toxicological effects on both animal and vegetal

life and humans have led to the regulation of these emissions by diverse national and trans-national organizations. Thus, the development of fast and reliable methods for the analysis of wastewaters is a topic of great interest and it is the subject of numerous studies.

The use of chemiluminescence (CL) as analytical technique is based on the measurement of the electromagnetic radiation (usually visible/near-infrared radiation) emitted by a chemical reaction, typically a reduction – oxidation reaction that produces radicals on an excited state. The most classical CL reaction is based on the oxidation of luminol (3-aminophthalhydrazide) with an oxidant

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(typically  $\text{H}_2\text{O}_2$ ) in alkaline medium, leading to light emission in the 425–435 nm range; other reactions use other oxidants as  $\text{MnO}_4^-$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $\text{IO}_4^-$ , among others, and reductants as  $\text{SO}_3^{2-}$ ,  $\text{NO}$  or organic compounds [1].

CL is characterized by high sensitivity and wide dynamic ranges, and it is usually measured in absence (or with low levels) of background light (“dark field” technique). This leads to very low detection limits compared to other optical techniques, being, in general,  $10^5$ – $10^3$  times more sensible than absorption and fluorescence techniques. On the other hand, CL technique also has some disadvantages. Thus, many CL reactions exhibit low selectivity, which leads to interference effects in methods without a separation stage. In addition, CL reactions usually have low robustness for many experimental conditions as pH, temperature, reagent concentrations, nature of solvent, ionic strength, etc. Likewise, CL emission is susceptible to quenching effects, so complex samples usually lead to notable matrix-effects on the results [2].

As has been previously mentioned, the most used CL reactions are based on the direct analyte oxidation or reduction or its catalytical effect on the CL reaction. This way, CL can be applied to the determination of some oxidants ( $\text{H}_2\text{O}_2$ ,  $\text{MnO}_4^-$ , etc.), sulfite or organic compounds as phenols (which lead to CL emission when oxidized in the adequate conditions), and inorganic cations with catalytical effect on luminol – oxidant reactions [1]. “Coupled reactions” methods, on the other hand, are indirect methods where the analyte participates in a chemical reaction that yields a product with a role in a CL reaction: for example, ethanol-alcohol oxidase reaction produces  $\text{H}_2\text{O}_2$  and it can be coupled to the luminol/ $\text{H}_2\text{O}_2$  CL reaction to analyze ethanol [3]. There are also methods based on the inhibition effect on a CL emission, due to quenching effect on the emitted light, the analyte reaction with one of the CL reagents (reducing its availability), etc. And finally, sensitized CL could be based on a chemical reaction that yields an excited product, inducing the excitation of the analyte (fluorophore) by a transfer-energy mechanism. This way, the reaction between oxalate diesters and  $\text{H}_2\text{O}_2$  yields excited peroxyoxalates which can participate in transfer-energy interactions with different fluorophores (pharmaceuticals, amino acids, PAHs, etc.) [4,5].

Electrochemiluminescence (ECL) methods are a more recent alternative to the previously mentioned mechanisms. These methods are typically based on the electrochemical generation of an ordinary

CL reagent or the electrochemical oxidation or reduction of the analyte in order to obtain a product to be used in a CL reaction. From an instrumental point of view, the main difference with respect to classic CL is the use of a modified measurement cell, which usually includes a three-electrode assembly (working, reference and counter electrodes) connected to a potentiostat [6,7].

CL can be measured using different device configurations. The simplest dynamic CL instruments are based on a flow-injection analysis (FIA) assembly where the reagents are pumped in different streams and measured in-situ in the detection cell. In some designs, one of these streams includes an injection system that allows the introduction of a discrete amount of a sample; in other cases, sample is continuously pumped into the system in one of the streams. This way, these configurations lead to transient and continuous CL emissions, respectively. Fig. 1 shows the scheme of a typical FIA-CL instrument, based on the mixture of two reagents (Channels A and B); the injection of the sample into one of the reagent streams is carried out by a 6-ways valve. The different streams are mixed into a flow-cell, and the CL emission is measured using a photomultiplier tube (PMT).

CL may also be coupled with a separation method as HPLC [8,9] or capillary electrophoresis (CE) [10,11], generating the CL emission by a post-column or post-capillar reaction. The advantages of the separation technique (the elimination of interferences from the matrix and the ability to quantify multiple analytes in a single run) are combined with the sensitivity of CL emission. The instrumental configuration is relatively simple: no light source is required (as in ultraviolet or fluorescence detection) and measurements are carried out only using a PMT, as in FIA configurations. On the other hand, mobile phase/carrier buffer must be carefully selected, in order to avoid possible interferences in the CL reaction or emission. Post-column configurations are preferred to pre-column ones in order to simplify the separation step. The most critical step to consider in post-column configurations is the mixing interface between the mobile phase (for HPLC) or buffer carrier (for CE) and the CL reagents streams. In many cases, these interfaces are homemade designed, and several operation modes have been proposed: flow-mixing, coaxial-mixing and reservoir-mixing between mobile phase and CL reagents, and off-column, on-column or end-column detection [12]. Fig. 2 resumes a simple HPLC-CL device that allows a gradient-elution HPLC separation

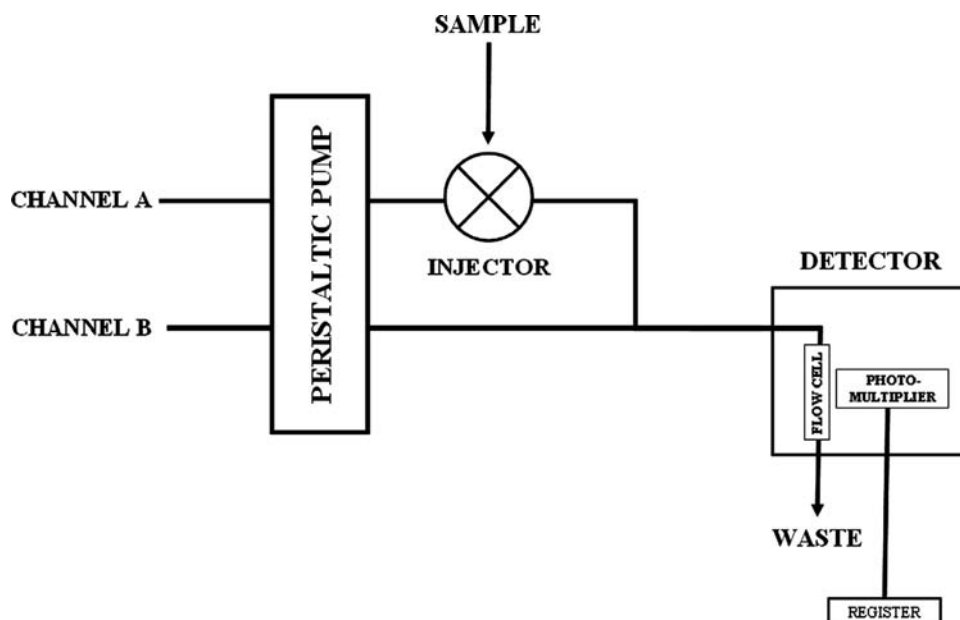


Fig. 1. Schematic diagram of a typical FIA-CL manifold.

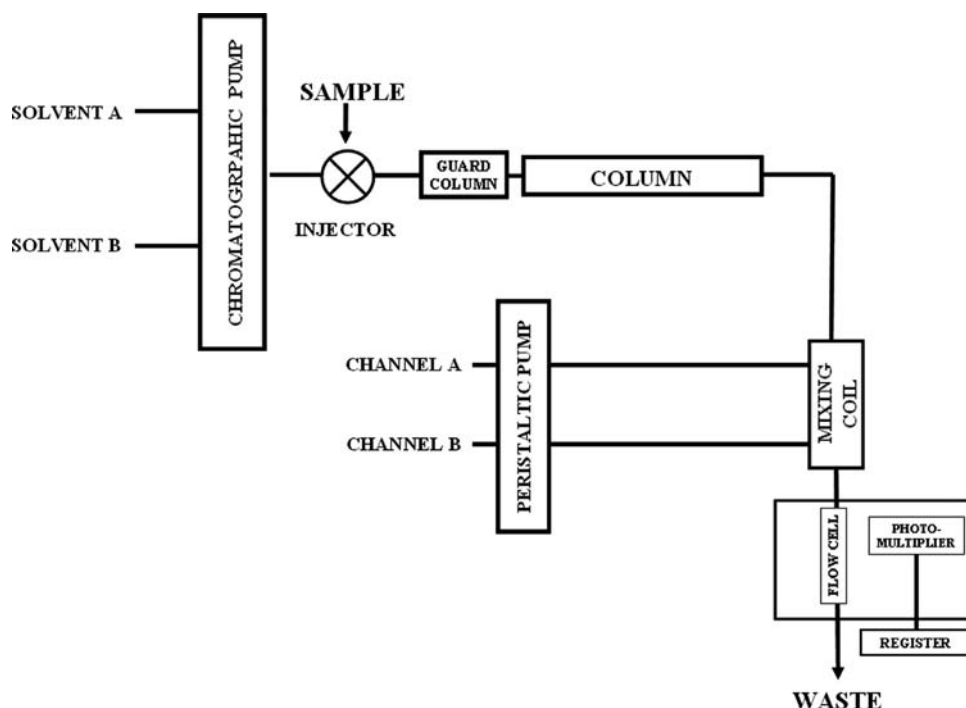


Fig. 2. Schematic diagram of a typical HPLC-CL manifold.

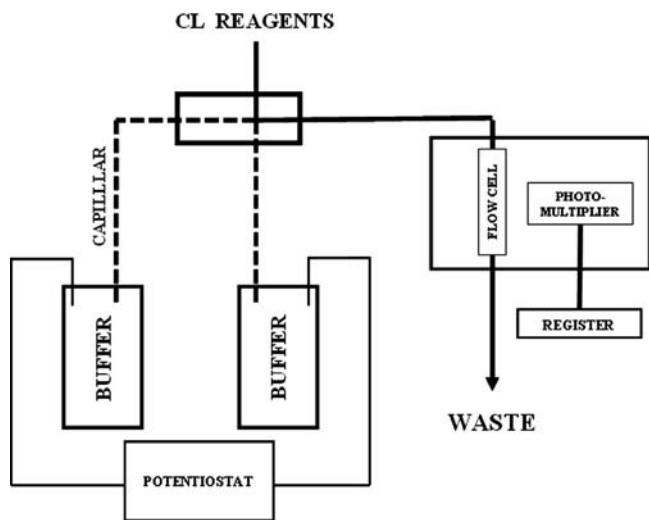


Fig. 3. Schematic diagram of a typical CE-CL manifold.

using two different solvents with FIA-CL detection; Fig. 3 shows the scheme of a CE-CL device based on off-capillary CL detection, with CL reagents directly mixed with the carrier-buffer stream (flow mixing) through a four-way connector.

CL can also be measured in gas-phase at high temperatures (High Temperature Oxidation-Chemiluminescence Detection, or HTO-CLD) for species as NO or SO<sub>2</sub>. These methods are usually based on the conversion of nitrogen/sulfur compounds in the sample to NO (by oxidation with O<sub>2</sub>) and SO<sub>2</sub> (by reduction with H<sub>2</sub>) and the reaction of these products with ozone, which leads to a CL emission. This procedure can be used as detection system for a gas chromatography separation or can be part of a FIA system [13,14]. Fig. 4 shows a typical scheme of this HTO-CLD experimental configuration.

In the last years, there has been an increasing interest in the development of CL sensors and biosensors in order to improve the selectivity of the technique. These efforts are usually hampered by

the short lifetimes of the obtained sensors. Nevertheless, different CL sensors have been developed, based on the immobilization of CL reagents on ion-exchange resins, the immobilization of enzymes on polymers (or sol-gels) or the application of new materials as nanoparticles, membranes, etc. [15]; also, several flow-through cell designs have been proposed for the integration of those sensors in FIA and CE systems [16].

CL methods have been widely applied to different analytical fields, as food analysis [17,18], pharmaceutical [19] and environmental analysis, including their application to the study of environmental waters [18,20,21]. A review concerning the application of CL in the analysis of traces of inorganic compounds in wastewater was published in 1996 [22]; this paper covers the application of CL in the determination of As, Cr, Mn, Co, V, Pb, and Cu. Another published review [23] discusses the application of CL in the analysis of wastewater from olive mill. The aim of this work is to carry out a comprehensive review of the application of CL in wastewater analysis with particular emphasis in different kinds of pollutants and discussing the described analytical and methodological approaches.

## 2. Determination of inorganic analytes

### 2.1. Determination of metals

Wastewaters from many different industrial processes often introduce high amounts of metals in different chemical and physical forms into the water cycle. Even if these metals are usually present in natural waters (underground or surface) at low levels, being in some cases essential element in biological systems at trace levels, their high concentrations usually led to toxic effects, both for vegetal and animal life-forms. Therefore, the monitoring of the emission of this species is a topic of great interest from the environmental and health-care point of view.

As can be seen in Table 1, a variety of methods has been applied for the determination of metals in wastewaters, FIA being the most common one.

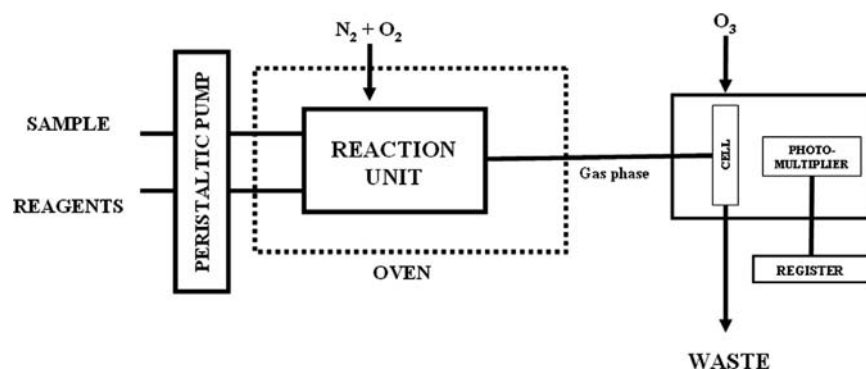


Fig. 4. Schematic diagram of a typical HTO-CLD instrument.

**Table 1**  
Chemiluminescence determination of inorganic analytes in wastewaters.

Analyte	Method	CL reaction	LOD	Reference
<i>Metals</i>				
Co(II)	FIA-CL	Luminol/H <sub>2</sub> O <sub>2</sub>	0.2 µg/L	[24]
Cr(VI)	FIA-CL	Luminol/H <sub>2</sub> O <sub>2</sub>	0.2 µg/L	[24]
Cu(II)	FIA-CL	Luminol/[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	8.0 × 10 <sup>-10</sup> M	[25]
Cu(II)	FIA-CL	Luminol/H <sub>2</sub> O <sub>2</sub>	3.2 × 10 <sup>-8</sup> M	[27]
Mn(II)	FIA-CL	Luminol/S <sub>4</sub> O <sub>8</sub> <sup>2-</sup>	1.0 × 10 <sup>-12</sup> M	[28]
Tl(III)	FIA-CL	Co(II)/H <sub>2</sub> O <sub>2</sub>	1.0 × 10 <sup>-6</sup> mg/mL	[29]
Co(II)	CL	Luminol/H <sub>2</sub> O <sub>2</sub>	9.15 × 10 <sup>-10</sup> mg/mL	[30]
Cr/U	CL	Luminol	<sup>a</sup>	[31]
Cu(II)	ECL	<sup>a</sup>	<sup>a</sup>	[32]
Cu(II)	ECL	g-C <sub>3</sub> N <sub>4</sub> /S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	0.9 × 10 <sup>-9</sup> M	[33]
Cu(II)	CE-CL	Luminol/[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	7.5 × 10 <sup>-9</sup> M	[34]
Co(II)	CE-CL	Luminol/[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	7.5 × 10 <sup>-11</sup> M	[35]
Cu(II)	CE-CL	Luminol/[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	7.5 × 10 <sup>-9</sup> M	[35]
Fe(II)	IC-CL	Luminol/H <sub>2</sub> O <sub>2</sub>	7 µg/L	[36]
Fe(III)	IC-CL	Luminol/H <sub>2</sub> O <sub>2</sub>	3 µg/L	[36]
<i>Non metals</i>				
S <sup>2-</sup>	FIA-CL	Tween80-rhodamine 6G	0.010 mg/L	[37]
S <sup>2-</sup>	FIA-CL	Luminol/H <sub>2</sub> O <sub>2</sub>	0.003 mg/L	[39]
Hydroxylamine	FIA-CL	Luminol/IO <sub>4</sub> <sup>-</sup>	4.0 × 10 <sup>-8</sup> M	[40]
NH <sub>3</sub> /NO <sub>3</sub> <sup>-</sup> /NO <sub>2</sub> <sup>-</sup>	FIA-CL	NO/O <sub>3</sub>	1 × 10 <sup>-8</sup> M	[41]

<sup>a</sup> Data not available.

This way, a stopped-flow method has been developed for Cr (VI) (previous reduction to its trivalent form) and Co (II) using their enhancing effect on the Luminol/H<sub>2</sub>O<sub>2</sub> CL reaction [24]. The simultaneous determination of both species is achieved by the application of two multivariate calibration models: Partial Least Squares (PLS) and H-point Standard Addition (HPSAM). This method takes advantage of the differences in the catalytic effect of these cations on the chemiluminescence reaction, as emission decay is faster for Co than for Cr, achieving their simultaneous determination without previous separation. As this procedure requires a time-resolved CL measurement, a stop-flow assembly is employed: this way, injected samples and reagents streams are initially mixed and, once sample reaches the detection cell, their flow is stopped to carry out the CL measurement. Both discrete and continuous sample injection are tested, with similar results for unicomponent determinations but better results for simultaneous determination in the second case. On the other hand, PLS and HPSAM provided similar results, both being useful for the proposed method.

The determination of Cu (II) in wastewaters has been carried out measuring its enhancing effect in the luminol/[Fe(CN)<sub>6</sub>]<sup>3-</sup> [25] using a

simple FIA system. The same authors have also found further enhancement in the CL emission in presence of 4-(2-pyridylazo)resorcinol for this analyte [26], plus other cations as Mn(II), Ni(II), Cr(III), etc.; this latter approach is not applied for wastewater analysis, but shows potential for it, with detection limits in the 10<sup>-9</sup>–10<sup>-8</sup> M range.

Another method for Cu(II) determination in wastewaters based on luminol/H<sub>2</sub>O<sub>2</sub> reaction has been proposed [27]. In this method, a cross-linked Cu<sup>2+</sup>-Chitosan imprinted resin is employed as CL sensor to achieve a pre-concentration and clean-up before the introduction of the sample the CL-detection system, allowing the study of complex samples. The preparation of the resin is based on the mixing of previously synthesized Cu(II)-Chitosan complex with glutaraldehyde and the further elution of Cu(II) from the obtained resin, which is then packed into a glass micro-column. The proposed method, thus, has four stages: initially, sample solution is continuously pumped into the resin, leading to the selective adsorption of Cu(II) in imprinted resin. Then, adsorbed Cu(II) is washed with water and eluted with luminol/H<sub>2</sub>O<sub>2</sub> (leading the corresponding CL emission). Finally, the resin is fully cleaned with a HCl solution in order to leave it ready for the next measurement. Authors found no significant variation in the obtained results after about 200 uses of the resin.

A method for the determination of Mn (II) based on its inhibition effect on the emission of the luminol/S<sub>4</sub>O<sub>8</sub><sup>2-</sup> reaction has been described [28]; this initially weak effect is enhanced in the presence of Ag<sup>+</sup>, which lead to low detection levels (Table 1).

Finally, an indirect method for the determination of Tl (III) in wastewaters has been proposed [29]. In this method, Tl (III) replaces the Co (II) in the Co (II) – EDTA complex. Liberated Co (II) is measured by its CL reaction with H<sub>2</sub>O<sub>2</sub> being the signal proportional to the amount of Tl (III) in the original samples.

With respect to non-flow injection analysis CL methods, CL in microemulsion conditions has been applied to the determination of Co (II) [30]. The presence of the surfactant increases the solubility of the reagents and their stability; this effect, added to the variation in the physical properties of the solution (polarity and viscosity), leads to an increase in the CL emission. Likewise, a CL method adapted for the measurement using portable luminometers has been developed for the determination of Cr and U ions, based on their reaction with luminol [31], allowing the in-situ monitoring of these ions in wastewaters.

ECL has been applied for the determination of Cu (II) in wastewaters, based on the CL enhancing properties of this cation [32] or in its quenching effect on ECL emission of graphite-like carbon nitride [33] in the presence of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>; the selectivity of this last approach allows the application of this material to design sensors for Cu monitoring. CL emission is based on the formation of excited C<sub>3</sub>N<sub>4</sub>\* from the electrochemically generated free radicals C<sub>3</sub>N<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>-</sup>. Potential interfering cations as Co (II), Zn (II),

K(I), Ca(II), etc., lead to non-significant quenching in the obtained ECL signal.

CL has been coupled to CE for the determination of some metallic cations in wastewaters. This way, the luminol/[Fe(CN)<sub>6</sub>]<sup>3-</sup> reaction has been applied for the determination of Cu (II) and Co (II) [34,35] after CE separation using a sodium acetate/acetic acid/ $\alpha$ -HIBA buffer as carrier solution. This detection system is based on an on-column coaxial flow design, where luminol is added into the carrier buffer solution and introduced at the head of separation capillary during electrophoresis. Separation is carried out in 6–7 min, with detection limits 1–2 order of magnitude lower than traditional CE systems, and 3 or more orders lower than ICP-AES. Nevertheless, the unambiguous identification and the quantitation of the analyte in complex wastewater samples show many difficulties, requiring the development of an adequate sample treatment process before its introduction in the CE system.

Ion Chromatography (IC) has been applied to the separation and determination of Fe (II) and Fe (III), previous complexation with pyridine 2,6-dicarboxylic acid (PDCA), with a CL-detection system based on the luminol-H<sub>2</sub>O<sub>2</sub> reaction [36]. The method is based on the separation of the Fe[PDCA]<sub>2</sub><sup>2-</sup> and Fe[PDCA]<sub>2</sub> complexes using a mixed-bed column (containing both anionic and cationic exchange sites with speciation capabilities for iron cations, among others) and a post-column mixing with luminol and H<sub>2</sub>O<sub>2</sub> streams. The separation is carried out in approximately 7 min, with better detection limits for Fe (II) than those achieved by spectrophotometric detection; the method, on the other side, is 1.4 less sensitive for Fe (III) than the spectrophotometric alternative. The method achieves the separation of Fe (II) and Fe (III) from other metals as Cd, Ca, Cr, Cu, Mg, Ni, Pb, and Zn.

## 2.2. Determination of non-metals

The bibliography concerning the application of CL in the determination of non-metallic inorganic analytes is scarce. This way, FIA has been applied to the determination of sulfide, measuring the emission obtained directly by the mixture of this analyte with Tween-80/Rhodamine 6G (Rh6G) [37]. This method is based on the reaction between sulfide and dissolved oxygen sensitized by (Rh6G) in presence of Tween-80 surfactant micelles; this way, the obtained excited SO<sub>2</sub><sup>-</sup> transfers its energy to Rh6G, leading to a CL emission with a maximum at 560 nm. The presence of a surfactant as Tween-80, on the other hand, enhances this energy-transfer process as it increases the solubility of Rh6G in the medium [38].

Another method for sulfide determination is based on its previous transfer as SH<sub>2</sub> with a gas diffusion system to the CL detector, measuring its catalytic effect on the luminol/H<sub>2</sub>O<sub>2</sub> reaction [39]. In this method, a multi-syringe system allows the online formation of SH<sub>2</sub> from the sulfide in the sample and its transfer across a polyvinylidene difluoride membrane to an alkaline solution, where it is converted again in sulfide and consequently injected into the CL-reagents streams. This way, sulfide is isolated from sample matrix before its measurement, allowing the elimination of many potential interferences. The method also achieves greater sensitivity, as the SH<sub>2</sub> transfer process also serves as a pre-concentration method (being the volume where SH<sub>2</sub> is converted back to sulfide significantly lower than the volume of treated sample).

Hydroxylamine has been measured by its enhancing effect on the weak luminol/IO<sub>4</sub><sup>-</sup> CL reaction, using a sensor based on an anion-exchange resin and a FIA system [40]. The sensor is prepared by dividing the resin in two parts and stirring them in luminol and periodate solutions. The obtained resins, after drying, are mixed and packed into a glass tube placed besides the detection window of a PMT. This way, once the sample is injected in the system, hydroxylamine reacts with luminol and periodate

(eluted from the ion exchange column), with the consequent CL emission. The authors found that the sensor could be reused for over 400 times without reproducibility lost.

A gas-phase CL method has been proposed for the determination of ammonia, nitrite and nitrate [41]. The method is based on the continuous injection of wastewater in the system, and the successive injection of discrete amounts of titanium (III) for nitrite and nitrate determination and hypochlorite for ammonium determination. These reagents allow the conversion of the analytes to NO, which is then measured using its gas-phase CL reaction with O<sub>3</sub> (as described in the Section 1). The method achieves a selective determination of the three analytes in the presence of other nitrogenous compounds (as urea, alanine or aspartic); on the other hand, high NaCl concentrations lead to a notable decrease in the CL signal, so corrective calibration actions must be carried out when the method is applied to high-salinity samples.

## 3. Determination of organic compounds

### 3.1. Phenol and phenolic derivatives

Phenols can be found in industrial wastewaters from several different processes: cooking plants, phenolic resins production, pesticides, paper and paint industries, among others. These compounds have high toxicity for both mammals and aquatic lifeforms, leading to liver and kidney damage, convulsions, or even death at high concentrations. Thus, many countries and international organism have established limits to the presence of these compounds in environmental waters [42–44].

As can be seen in Table 2, in the last years some methods for the determination of phenols in wastewaters have been proposed. Most of these methods are based on FIA with CL detection technique, and only in some cases CL has been coupled with a separation technique. A HPLC-CL method for the simultaneous determination of phenol and N,N-dimethylaniline in dyestuff wastewater has been proposed [42]. The method is based on the separation of both analytes using an isocratic ethanol/0.01% triethylamine mobile phase and a C18 column; detection is carried out by a post-column reaction with luminol/ferricyanide. The sensitivity of this procedure is similar to those achieved in HPLC-UV determinations of these analytes; also, the method has limited sensitivity for potential interferences as aromatic amines. CL detection has also been coupled to CE separation for the determination of benzenediol isomers and phenol in coke plant wastewater [45]; the method is based on the inhibition effect of these analytes on the luminol/ferricyanide CL reaction. Nevertheless, some of the FIA-CL methods include in their device design the use of an on-line pre-concentration/clean-up stage a solid-phase extraction resin as C18-modified silica gel [43] or XAD-4 [46]. Also, a CL method in static conditions has been proposed for the determination of the antioxidant-activity index/total phenols for olive-mill wastewaters [47], based on phenols inhibition effect in the CL Co(II)/H<sub>2</sub>O<sub>2</sub> reaction. The method is carried out by direct mixing in a glass cuvette and measuring in a lamp-off fluorimeter. This procedure is applied for wastewater from different olive-oil milling procedures (three-phase and two-phase), in order to compare their potential pollutant risks. Higher total phenol amounts were found when three-phase olive oil extraction procedures were applied. The obtained results were comparable to those obtained using the Folin-Ciocalteu method.

Proposed methods based on the use of FIA-CL configurations use several CL reactions with varied mechanism. Some methods are based on the direct measurement of the emitted light from the oxidation of the phenolic molecule by permanganate [46,48–50], chlorate [51] or cerium [52]. Nevertheless, as can be seen in

**Table 2**  
Chemiluminescence determination of phenols in wastewaters.

Analyte	Method	CL reaction	LOD	Reference
Phenol	HPLC-CL	Luminol/[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	2.5 × 10 <sup>-8</sup> g/mL	[42]
Phenol	FIA-CL	Luminol/[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	0.66 ng/L	[43]
Phenol	FIA-CL	Luminol/H <sub>2</sub> O <sub>2</sub> /Hemin <sup>a</sup>	0.4 ng/mL	[44]
Benzediyol isomers, phenol	CE-CL	Luminol/[Fe(CN) <sub>6</sub> ] <sup>3-a</sup>	2.8 × 10 <sup>-8</sup> –4.4 × 10 <sup>-6</sup> M	[45]
Phenol	FIA-CL	Fenol/MnO <sub>4</sub> <sup>-</sup>	5.0 ng/mL	[46]
Phenols (antioxidant index)	CL	Luminol/Co(II)/AEDT		[47]
Phenols	FIA-CL	Fenol/MnO <sub>4</sub> <sup>-</sup>	1.2 × 10 <sup>-6</sup> M	[48]
Resorcinol	FIA-CL	Resorcinol/MnO <sub>4</sub> <sup>-</sup>	0.06 µg/mL	[49]
Phenol	FIA-CL	Fenol/MnO <sub>4</sub> <sup>-</sup>	3 × 10 <sup>-9</sup> g/mL	[50]
Phloroglucinol	FIA-CL	Phloroglucinol/KClO <sub>3</sub> <sup>c</sup>	3.9 × 10 <sup>-3</sup> µg/L	[51]
Catechol	FIA-CL	Catechol/Ce(IV) <sup>b</sup>	1.0 × 10 <sup>-7</sup> M	[52]
Hydroquinone	FIA-CL	Luminol/IO <sub>4</sub> <sup>-</sup>	8.2 × 10 <sup>-10</sup> M	[53]
Phenol	FIA-CL	MnO <sub>4</sub> <sup>-</sup> /H <sub>2</sub> O <sub>2</sub>	3 × 10 <sup>-5</sup> g/L	[54]
Pyrocatechol	FIA-CL	Galangin/MnO <sub>4</sub> <sup>-</sup>	1.0 × 10 <sup>-8</sup> M	[55]
Pyrogallol	FIA-CL	Luminol/IO <sub>4</sub> <sup>-</sup>	0.78 µg/L	[56]
Resorcinol	FIA-CL	Luminol/[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	5.7 × 10 <sup>-9</sup> kg/L	[57]
Tannic acid	FIA-CL	IO <sub>4</sub> <sup>-</sup> /H <sub>2</sub> O <sub>2</sub> <sup>b</sup>	2.3 × 10 <sup>-9</sup> M	[58]
Tannic acid	FIA-CL	Luminol/[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	1.0 × 10 <sup>-10</sup> M	[59]
p-aminophenol	FIA-CL	Luminol/DMSO/NaOH/EDTA <sup>a</sup>	1.9 × 10 <sup>-10</sup> g/mL	[60]
p-aminophenol	FIA-CL	Luminol/DMSO/NaOH/EDTA <sup>a</sup>	1.9 × 10 <sup>-10</sup> g/mL	[61]
Phenol	FIA-CL	Luminol/H <sub>2</sub> O <sub>2</sub> /CdS <sup>a</sup>	2.5 × 10 <sup>-9</sup> g/L	[62]
Tannic acid	FIA-CL	Luminol/H <sub>2</sub> O <sub>2</sub> <sup>a</sup>	5.6 × 10 <sup>-11</sup> M	[63]

<sup>a</sup> Inhibited by the analyte.<sup>b</sup> Measurements are carried out in Tween 40 medium.<sup>c</sup> Measurements are carried out in sodium dodecyl benzene sulfonate medium.**Table 3**  
Chemiluminescence determination of other organic compounds in wastewaters.

Analyte	Method	CL reaction	LOD	Reference
Aluminum L-lactate	FIA-CL	MnO <sub>4</sub> <sup>-</sup> /H <sub>2</sub> SO <sub>4</sub> /Au nanoparticles	1.04 × 10 <sup>-6</sup> g/mL	[64]
5-Sulfosalicylic acid	FIA-CL	Luminol/MnO <sub>4</sub> <sup>-</sup>	3.8 × 10 <sup>-6</sup> M	[65]
5-Sulfosalicylic acid	FIA-CL	N-bromosuccinimide/dichlorofluorescein	1.0 × 10 <sup>-8</sup> M	[66]
5-Sulfosalicylic acid	FIA-CL	Luminol/H <sub>2</sub> O <sub>2</sub> /Ag nanoparticles	1.0 × 10 <sup>-9</sup> M	[67]
5-Sulfosalicylic acid	FIA-CL	5-sulfosalicylic acid/MnO <sub>4</sub> <sup>-</sup> /glyoxal	2.0 × 10 <sup>-9</sup> M	[68]
5-Sulfosalicylic acid	FIA-CL	Luminol/pyrogallol	6.8 × 10 <sup>-8</sup> M	[69]
17β-Estradiol	CL	Luminol/H <sub>2</sub> O <sub>2</sub>	2.0 pg/mL	[71]
17β-Estradiol	CL	AMPPD/ALP	1.5 pg/mL	[72]
Humic acid	FIA-CL	Ce(IV)/H <sub>2</sub> SO <sub>4</sub> /rhodamine 6G	3 µg/L	[73]
N,N-dimethylaniline	HPLC-CL	Luminol/[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	1.2 × 10 <sup>-8</sup> g/mL	[42]
N-nitrosamines	HPLC-CL	Luminol/NO	1.5–3.0 ng/L	[74]
Metoclopramide	FIA-CL	Metoclopramide/MnO <sub>4</sub> <sup>-</sup>	0.1 mg/L	[75]
Acetaldehyde	FIA-CL	Gallic acid/H <sub>2</sub> O <sub>2</sub>	3.1 × 10 <sup>-8</sup> M	[76]
Formaldehyde	FIA-CL	Ninhydrin/MnO <sub>4</sub> <sup>-</sup>	4.6 × 10 <sup>-4</sup> µg/mL	[77]

Table 2, most of these methods are based on the effect of phenols on the enhancement [43,53–59] or inhibition [44,60–63] of the redox-reaction. As a rule, these methods achieve better detection limits than traditional HPLC techniques, but their main advantage over the former methods can be found in their selectivity, allowing the determination without separation and, thus, with lower time of analysis.

### 3.2. Other organic compounds

Besides the methods for phenol determination described in the previous section, CL has been applied for the determination of other organic compounds of varied nature, as can be seen in Table 3.

Aluminum L-lactate is used as a reagent or raw material in different industries as food production or pharmaceuticals. A method for the determination of this compound is based on its CL reaction with MnO<sub>4</sub><sup>-</sup>/H<sub>2</sub>SO<sub>4</sub> in presence of gold nanoparticles [64], allowing the determination in acidic medium without previous derivatization, unlike traditional CL systems. The method

**Table 4**  
Chemiluminescence determination of non-specific parameters in wastewaters.

Parameter	Method	CL reaction	Reference
BOD	CL	Luminol/H <sub>2</sub> O <sub>2</sub>	[78]
COD	CL	MnO <sub>4</sub> <sup>-</sup> /glutaraldehyde	[79]
COD	FIA-CL	Luminol/MnO <sub>4</sub> <sup>-</sup>	[80]
COD	CL	Luminol/H <sub>2</sub> O <sub>2</sub>	[81]
COD	CL	Luminol/H <sub>2</sub> O <sub>2</sub>	[82]
COD	CL	Luminol/organic compounds	[83]
TOC,TIC	FIA-CL	Luminol/H <sub>2</sub> O <sub>2</sub>	[84]
TN	HTO-CLD	NO/O <sub>3</sub>	[85]
TN	HTO-CLD	NO/O <sub>3</sub>	[86]
TOC,TN	HTO-CLD	NO/O <sub>3</sub> (TN)	[87]

takes advantage of the aggregation capability of Au nanoparticles with organic compounds with –OH groups (as lactate) and the catalytic effect of these nanoparticles on CL reactions involving the oxidation of these species (Table 4).

5-Sulfosalicylic acid is an organic molecule whose main application is to serve as a raw material for the production of pharmaceuticals [65–69]. This substance can be found in wastewaters associated to active pharmaceuticals as doxycycline [65–68] or oxycycline [69]. As can be seen in Table 3, a series of FIA-CL methods based on different CL reactions have been developed for the determination of 5-sulfosalicylic acid. These methods are usually based on the enhancing effect of this molecule over the emission signal of a well-established CL reaction, (except in the luminol/pyrogallol case [69] where CL is inhibited by the presence of the analyte). As an additional note, one of these methods [67] uses Ag nanoparticles to further enhance the CL of luminol/H<sub>2</sub>O<sub>2</sub> system, as they exhibit similar catalytic properties to those previously described for Au nanoparticles [70].

17 $\beta$ -Estradiol (E2) is an estrogen sex hormone and endocrine disruptor whose presence could lead to several adverse malfunctions and carcinogenic effects in wildlife and humans. A CL method [71] for the determination of this specie in wastewaters is based on the immobilization of the analyte in magnetic particles labeled with the specific anti-E2 polyclonal antibody as extracting agent. The CL is based on the reaction of luminol with the H<sub>2</sub>O<sub>2</sub> obtained from the addition of peroxidase to the extracted analyte. Another method [72] is based on the immobilization of the anti-E2 antibody on a fluorescein-iso-thiocyanate (FITC)-anti-FITC solid substrate. Measurement is carried out in two steps; the first stage involves a competitive reaction between the immobilized anti-E2 antibody and both E2 (from the sample) and biotin-E2 (added as a reagent). In a second stage, ALP and AMPPD are successively added to the mixture; their reaction with the with the biotin-E2 (bonded to the anti-E2 antibody in the previous stage) leads to the corresponding CL emission. Obtained CL signal has an inverse relationship with analyte concentration, as higher concentrations of E2 in the sample lead to less available biotin-E2 when CL reaction is carried out. Both methods have sensitivities comparable to those achieved by traditional ELISA measurements (1.5–2.5 pg mL<sup>-1</sup>), but the luminol/H<sub>2</sub>O<sub>2</sub> method requires lower total assay times (around 45 min) than the ALP/AMPPD method (higher than 10 h).

Humic acids (a complex mixture of organic acids from the biodegradation of bioorganic material) have been measured by its enhancing effect on the Ce(IV)/H<sub>2</sub>SO<sub>4</sub>/rhodamine 6G CL reaction [73]. The method includes an on-line clean-up/preconcentration stage using polar-enhanced polymer particles packed in a SPE cartridge (directly installed in the injection manifold). The method can be applied for the continuous monitoring of environmental waters. On the other hand, it was found that the presence of phenols in the sample leads to important interference effects, so the method has limited application to wastewaters with high concentrations of these species.

CL has been applied to the determination of diverse amines by coupling a CL detection system to HPLC separation. N,N-dimethylaniline (simultaneously with phenol, as described previously) [42] has been determined in wastewaters after HPLC separation with a C18 column. N-nitrosamines [74] have been also measured with a CL method based on the generation of NO by ultraviolet irradiation after chromatographic separation. In order to achieve this, a photochemical reactor based on a low-pressure mercury lamp and a reaction coil are placed after the HPLC column. Eluted analytes are UV-irradiated for 15 sec before mixing with a luminol solution stream in the reaction coil, with the subsequent CL reaction between generated NO and luminol. The method shows adequate sensitivity in the determination of N-nitrosamines. Other nitrogenous compounds as nitrite, nitrate or nitrobenzene, lead to lower CL emission (or negligible in the case of molecules as diethylamine and ammonium) due to the lower efficiency in photochemical NO generation for these species; nevertheless,

higher irradiation times could be applied in order to obtain acceptable signals for some of these compounds.

Finally, CL has been applied for the determination of other miscellaneous organic species in wastewaters using a typical FIA-CL configuration scheme, with comparable results to those achieved by HPLC-UV or other traditional methods. The antiemetic and gastroprokinetic agent metoclopramide has been determined in wastewaters using the generated CL by its direct oxidation with permanganate (enhanced by the presence of formaldehyde) [75]. Also, acetaldehyde [76] and formaldehyde [77] have been measured by its enhancing effect on gallic acid/H<sub>2</sub>O<sub>2</sub> and ninhydrin/permanganate reactions, respectively.

#### 4. Determination of non-specific parameters

In addition to its application for the determination of organic and inorganic species of diverse nature, CL has also been applied to the estimation of non-specific parameters with great importance in the assessment of the quality of waters or the monitorization of pollutant emissions.

##### 4.1. Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD)

Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) are two arbitrary empirical parameters traditionally used for the monitoring and quality-assessment of waters. COD represents the amount of oxygen consumed by the oxidation of the organic compounds present in the samples to their respective inorganic end products, while BOD is associated to the oxygen used by the biological organism in the sample to carry out this oxidation [78,79]. The reference methods for COD determination are based on the addition of a known amount of an oxidant (as potassium permanganate or potassium dichromate) in acid solution under established conditions and the measurement of the oxidant leftover after the sample digestion.

CL methods for COD determination can be based on the measurement of the oxidant leftover by taking advantage of its role in a CL reaction as oxidant. This approach has been applied for COD determination in wastewaters using permanganate as oxidant by measuring the CL emission of permanganate/glutaraldehyde [79]. In this method, digested samples are placed in a multiple-well plate on the top of a movable plate carrier. Glutaraldehyde is successively added in the different wells, and its reaction with MnO<sub>4</sub><sup>-</sup> leftover produces a CL emission that is measured by a PMT. Another method is based on the reaction of MnO<sub>4</sub><sup>-</sup> leftover with luminol by injection of the digested sample in a FIA system in [80]. Both methods show similar detection limits (0.1–0.3 mg/L), but the glutaraldehyde method can be easily automated, with higher throughput (3 × 96 samples per hour, compared with 60 samples per hour for the luminol method).

Another approach for COD determination is based on the catalytical effect of oxidant leftover on a CL reaction. This way, the catalytical effect of Cr (III) on the luminol/H<sub>2</sub>O<sub>2</sub> CL reaction has been applied to the determination of COD, using dichromate as oxidant for the digestion process and reducing its leftover to Cr (III) [81]. This approach has also been applied to design a home-made polymethyl methacrylate micro-flow CL system on a 50 × 40 mm<sup>2</sup> chip for COD determination [82]. The method is notably faster than traditional digestion, as the micro-flow system allows the on-line digestion and CL measurement of the sample. Likewise, the short reaction time increases the selectivity of the method, as the probability of side reactions between oxidant and potential interferences is reduced.

An alternative method for COD determination in wastewaters that replaces the use of traditional oxidants by CdTe quantum dots has been proposed [83]. This method uses a FIA configuration where wastewater sample is continuously injected and mixed with the CdTe carrier solution. The combined streams are then sent to a photo-irradiation unit (a reaction coil under a quartz UV lamp), where CdTe nanocrystals generate strong oxidation agents to degrade the organic compounds in the sample, producing OH<sup>-</sup> radicals. In the last stage, obtained OH<sup>-</sup> is measured using its CL-reaction with luminol. This method reduces notably the analysis time to lower than 2 min per sample, compared with the several hours per sample required by traditional methods.

BOD estimation is typically based on the measurement of dissolved oxygen both before and after the bioorganic decomposition of a substrate. As an alternative, CL has been applied to BOD determination in wastewater [78]. The method is based on the measurement of the active oxygen species such as superoxide anions and hydrogen peroxide (employing their CL-reaction with luminol, catalyzed by ferricyanide) obtained from the decomposition of the naphthoquinone menadione by *Saccharomyces cerevisia*. CL is measured in static conditions, mixing the incubated sample with the CL reagents in a transparent polystyrene tube and measuring the obtained light emission for 15 sec. This method improves the sensitivity of the traditional procedures at least by 10 times; nevertheless, the obtained results are notably influenced by the presence of several ions (as Cr<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, etc.). This is an important limitation to the application of the method to wastewater analysis, as the concentrations of these metallic ions are usually very high.

#### 4.2. Total organic carbon and inorganic carbon (TOC and TIC) and total nitrogen (TN)

Total inorganic carbon (TIC) and total organic carbon (TOC) are two global indicators whose estimations show a significant interest in pollution control. Traditionally, the estimation of these parameters is based on the measurement of the CO<sub>2</sub> obtained from the decomposition of the sample with acids (TIC) or from its wet or dry combustion (TOC). As an alternative, a FIA-CL method [84] has been proposed, based on the wet chemical oxidation of wastewater samples with phosphoric acid (TIC) or potassium hydroxide (TOC), collecting the obtained gaseous CO<sub>2</sub> as carbonate in an alkaline solution. Once oxidation is completed, the carbonate solution is pumped into a FIA-CL system, taking advantage of the enhancing effect of this molecule on the luminol-H<sub>2</sub>O<sub>2</sub> CL-reaction. The method has high selectivity, as the collection of carbon in gaseous isolate the analyte of potential interferences (as cationic metals). The presence of other volatile chemicals which could be generated during the oxidation stage (H<sub>2</sub>S, HF, NO<sub>2</sub>, etc.) shows no significant effect on the results. On the other hand, samples with lower than 0.08 mg/L TOC levels show incomplete carbon oxidation, making the obtained recoveries lower than expected.

Total nitrogen (TN) is a parameter of significant importance in wastewaters, due to the eutrophication effect of polluted waters rich in nitrogen-compounds. This parameter has been traditionally measured by the application of the Kjeldahl method, Devarda's alloy method (where nitrogen in NO<sub>2</sub><sup>-</sup>/NO<sub>3</sub><sup>-</sup> form is reduced to NH<sub>4</sub><sup>+</sup> with a Cu/Al/Zn 50:45:5 alloy in sulfuric acid and potassium sulfate medium) [85] or some variation of them. HTO-CLD has been proposed as an interesting alternative [85,86]. Wastewater samples are heated to 720 °C in the presence of adequate catalysts to produce NO by the oxidative pyrolysis of the chemically bound nitrogen in the samples. Then, the sample is treated with ozone to generate the metastable and chemiluminescence NO<sub>2</sub><sup>\*</sup>. The obtained results are similar to those obtained with the traditional Devarda alloy method, showing greater precision and lower analysis times.

TOC and TN have been simultaneously measured in wastewater by coupling a TOC analyzer with a HTO-CLD system, as detailed above [87]. The authors observed that the direct injection of high-particulate matter content (as domestic wastewater) led to non-acceptable N-recovery rates, as the presence of these particles interfered with the evaporation step. This interference was solved by the application of a pyrolytic stage at 690 °C (injecting the sample on a 1-cm thick quartz wool pellet on top of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst). The obtained results are comparable to those obtained by wet digestion procedure.

## 5. Conclusions and future perspectives

To date, as discussed in the previous sections, CL methods have proved to be a useful tool for the analysis and monitoring of some of the most typical pollutants that can be found in wastewater samples. Additionally CL can be used for the determination of non-specific but very interesting water parameters. CL could be an interesting alternative in order to develop simple, fast and low cost methods for the analysis of other species in wastewater as, for example, emerging pollutants as phthalates, Bisphenol A and pharmaceuticals (among others) [88].

Nevertheless, low selectivity and robustness often lead to limited applicability of CL technique to complex wastewater samples. These shortcomings can be overcome by coupling with a separation method (as HPLC or CE), but, in this case, some of the most interesting advantages of CL technique (fast analysis and simple instrumentation) would be lost. So, in order to extend the range of application of this technique, improvements in both technique selectivity and procedure robustness should be achieved to minimize the influence of the presence of other species in the sample. This way, the development of new CL sensors and lab-on-a-chip technology [89,90] can achieve analyte separations (usually with a miniaturized electrophoresis system) [91] without the need of complex instrumentation.

Finally, as an alternative, the inclusion of a microextraction step in sample pretreatment shows great potential, as these procedures typically achieves great (and, many times, selective) preconcentration of the analyte and in most cases an effective clean-up of the sample avoiding potential interferences [92,93].

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