Fluorescence and Phosphorescence Chemical Sensors Applied to Water Samples

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Abstract. Due to the outstanding characteristics of both fluorescence and phosphorescence signals, they are widely applied to the construction of chemical sensors. The development of these sensors for the detection and quantification of compounds of environmental concern is an active research topic, daily enriched with the contribution of new works in the area. This chapter provides fundamentals and practical aspects of this type of sensors, focusing in those works devoted to quantify both organic and inorganic pollutants in environmental waters. The chapter is organized upon the basic functional units of a chemical sensor. A few examples of strategies of evaluation involving multivariate chemometric analysis are also discussed.

Keywords: Fluorescence, phosphorescence, chemical sensors, pollutants, natural waters.

1 Introduction

The definition of a chemical sensor is ambiguous, and different concepts have been proposed in the scientific literature. Many researchers of the sensor community indicate that sensing refers to a continuous process (i.e., continuously recording) of detection, and agree with the Cambrigde definition which states: "C*hemical sensor is a miniaturized device that can deliver real-time and on-line information on the presence of specific compounds or ions even in complex samples"* [1,2]. Similarly, Gauglitz considers that a complete sensor system involves a sensitive layer, transduction (recognition) principles, the signal processing and the strategies (software) of evaluation [3], and Janata suggests that the term "chemical sensor" should be restricted to those devices which acquire information *continuously*, while sensing systems which obtain information in *discrete steps* should be named as "analytical assays" [4]. These specifications are made because the term "sensor" is often used to refer to a probe or indicator (molecule or nanoparticle) that communicates the presence of an analyte *via* modulation of an analytical signal [5].

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S.C. Mukhopadhyay & A. Mason (Eds.): *Real-Time Water Quality Monitoring*, SSMI 4, pp. 45–64.
DOI: 10.1007/978-3-642-37006-9_3 © Springer-Verlag Berlin Heidelberg 2013

Valcarcel and Luque de Castro [6] define a chemical sensor as a device providing information about the system under study through the integration of a transducer (optical, electroanalytical, thermal, etc.) with a microzone where a chemical reaction takes place. This device can result in either a "probe" [able to sense the analyte in batch mode (single-shot) or in a flow-system (continuous recording)], or in a flow-through sensor (continuous recording). Finally, according to IUPAC, "*A chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. The chemical information mentioned above may originate from a chemical reaction of the analyte or from a physical property of the system investigated*" [7]. Fig.1 summarizes some configurations and sensing modes.

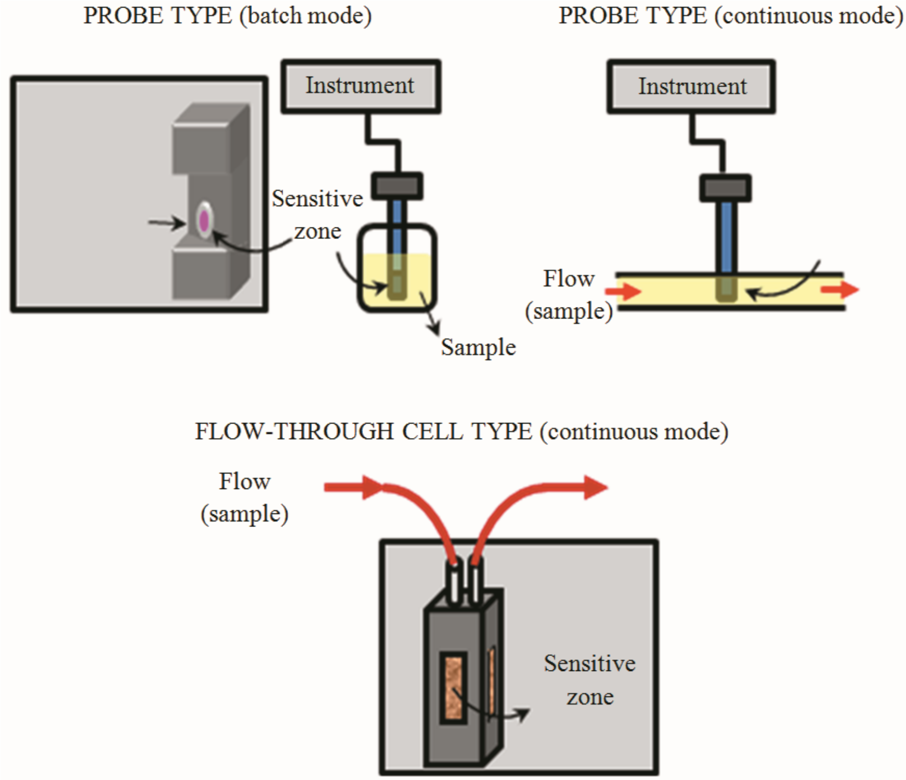

Fig. 1. Schematic representation of different configurations and optosensing modes

The dissimilarities in sensor definitions makes it difficult to provide a classification that covers all involved aspects (e.g. type of measured signal, external shape, sensing scheme, platform employed, etc.). Generally, the designation of a sensor is related to both the area of investigation where the sensor will be applied and to the concept of sensor adopted by the analyst. Fortunately, all researchers agree with a classification based on the transduction mechanism which categorizes sensors in electrochemical, optical (absorbance, reflectance, chemoluminescence, luminescence, refractive index, optothermal effect and light scattering signals), electrical, mass sensitive, magnetic, thermometric and based on other physical properties [7]. In addition, several characteristics may be indicated: probes or flow-through sensors [8], portable/ handheld or not [9,10], optical fibers-based and planar waveguide systems, direct (the measured signal corresponds to an intrinsic optical property of the analyte) or reagent-mediated (an auxiliary reagent is needed to detect the analyte presence). In many cases, the immobilization approaches in both direct and reagent-mediated sensors are indicated in the name of the sensor (*e.g.* sol-gel based sensors, polymer based sensors, molecularly-imprinted polymer (MIP) sensors, etc.). Classifications can be complementary and it would be desirable to avoid a rigid scheme, trying to cover most principles involved in the nature of the sensor under study. IUPAC considers that chemical sensors contain two basic functional units: a *receptor* part and a *transducer* part. In the receptor part the chemical information is transformed into a form of energy, which is measured by the transducer, where the energy is transformed into a useful analytical signal [7].

Due to the many advantages of optical sensors, such as sensitivity, versatility, possibility of on-line detection and miniaturization, among others, they are of great utility in the environmental area, and numerous publications devoted to their application for the determination of compounds of environmental concern have been discussed in the literature [11-15].

This chapter deals with luminescent sensors and probes reported in recent years for the determination of both organic and inorganic pollutants, focusing the attention mainly in the above mentioned basic functional units, which have suffered significant changes over the years. However, a few examples of new strategies of evaluation will be treated. Neither sensing systems, which only involve measurements of signals produced by a chemical reaction in solution, nor bio-sensors are included in this chapter. The organization adopted is shown in Fig. 2, and includes both probes and complete chemical sensor systems. In this figure, planar waveguide systems [2] have been omitted as transduction platforms because most of them are based on biological reactions [16], which are beyond the scope of this chapter.

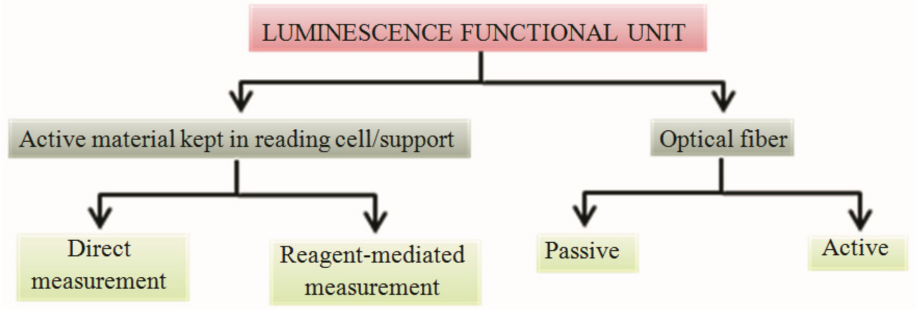

Fig. 2. Organization of the chapter

2 Active Material Kept in Reading Cell/Support

2.1 Direct Measurement

In this case, the emitted luminescent signal is directly measured after the analyte is retained in a suitable solid support [6,17-19]. In probe configurations, the analyte is retained by adsorption, binding or entrapment, either on a plane surface or in microbeads. The deposit of the analyte in plane surfaces can be carried out by different procedures. One possibility is spotting a few microliters of the sample in the support with the aid of a micropipette (Fig. 3A). A convenient mode of both retaining and simultaneously preconcentrating the analyte is to perform a solid-phase extraction procedure (Fig. 3B). In this case, the active support is a disk loaded into a stainless steel filter holder, and placed into a syringe. Through manual or mechanic positive pressure, the sample solution is forced through the membrane and analytes are retained on its surface.

After immobilization, plane surfaces are placed in an appropriate reading cell/support. Solid-sample holder accessories are commercially available and are adequate for thin films, powders, pellets and fibers. However, there are other experimental approaches which can be implemented for reading from solid supports. For example, if the sample is spotted in a sheet of paper or membrane, the surface can be located in a conventional fluorescence cell in a correct position to measure either reflection or transmission of the fluorescence signal (Fig. 4A). The layer can also be located between two quartz sheets and then in a chamber for spectrofluorimetric measurements (Fig. 4B). Disks used in solid-phase extraction can be placed in laboratory constructed holders, or in capped cells with nitrogen bubbling, for example, for phosphorescence measurements (Fig. 4C).

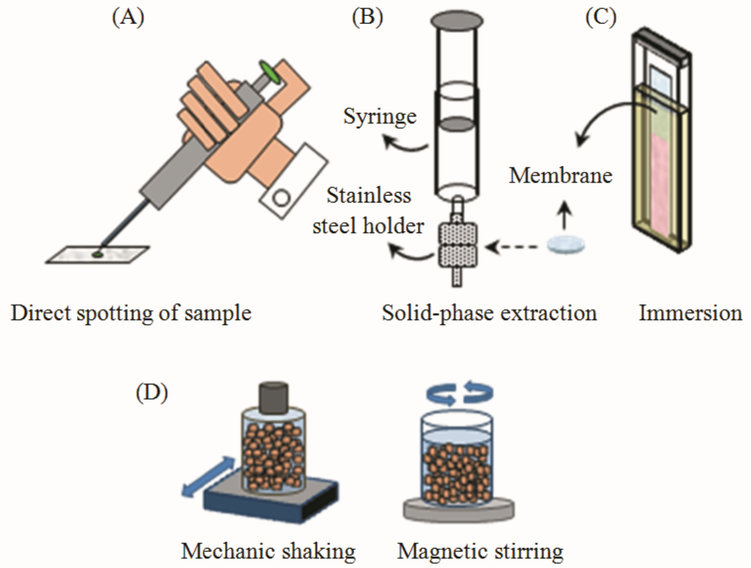

Fig. 3. Some experimental modes for immobilize the analyte in probe configurations. (A-C) plane surfaces, (D) microbeads.

As will be shown below, plane supports can also be set in laboratory-constructed special holders for performing determinations in flow-systems.

When particulate materials are used as probes, equilibrium is established between microbead active sites and the analyte (Fig. 3C). Beads are then transferred to a specially designed spectrofluorimetric holding. On the other hand, in flow-through optosensors, microbeads are contained in a flow-cell. In simpler configurations, a carrier solution transports the sample containing the analyte in a continuous flow system. When the analyte reaches the solid support filling the flow-cell, its on-line immobilization is produced and its luminescence signal is measured.

Filter-papers were common plane-supports used in the first works on solid-phase luminescence (SPL) and were gradually replaced by other materials, such as C18-disks, nylon membranes and polymeric membranes, with improved sensor qualities. Nylon membranes showed to be adequate film supports for the phosphorescence quantification of thiabendazole in natural waters [20]. Based on a solid-phase extraction on a nylon membrane, benzo[*a*]pyrene was determined through both fluorescent and phosphorescent measurements at sub-parts-per-trillion (sub-ng L^{-1}) levels in spiked tap, underground and mineral water samples of different origins [21]. Besides, polymeric materials, ion-exchange resins, bonded-phase silicagel [22] and nylon powder, among others, are employed in manufacturing microbeads and filler particles. Salinas Castillo *et al* presented the phosphorescence characterization of polycyclic aromatic hydrocarbons (PAHs) using non-ionic resins. The study allowed them to develop a flow-through phosphorescence optosensor for the selective determination of benzo(*a*)pyrene [23].

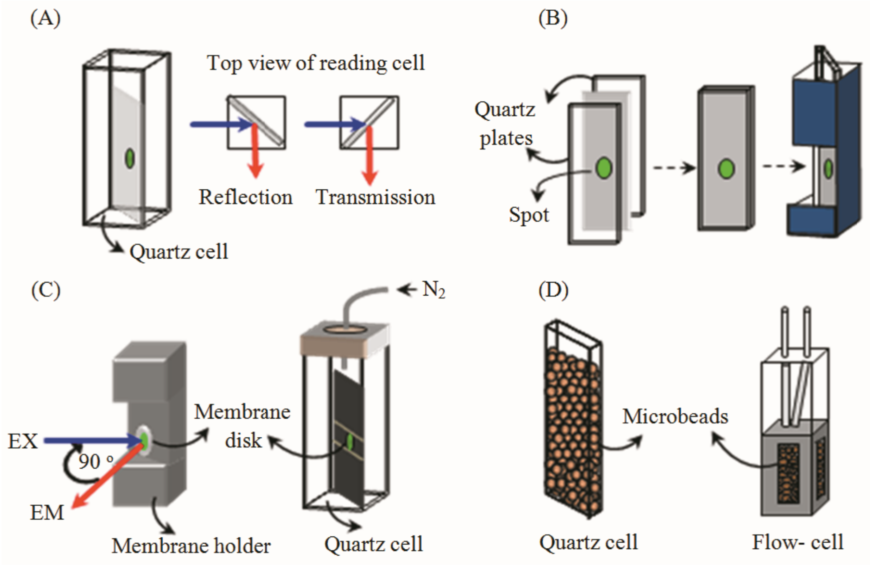

Fig. 4. (A-B) Fluorescence reading configurations for planar spotted surfaces. (C) Disks holder configurations. (D) Microbead holders for probe and flow-through optosensors.

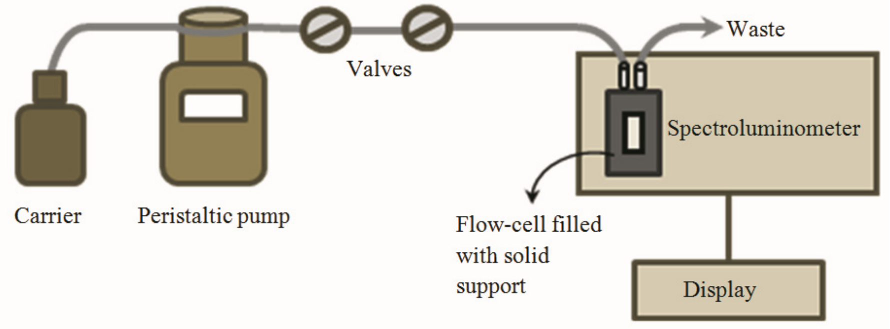

Fig. 5. Scheme of a flow-through luminescence sensor

MIPs are materials containing cavities capable of binding the analyte through a selective recognition, and are being increasingly used as solid-supports, especially when determinations are carried out in complex matrices where selectivity is mandatory [24-27]. MIPs are used in flow-through optosensor and in fiber-optic configurations (see below). Microbeads, powders and MIPs are adequate materials to pack a spectrofluorimetric cell coupled to a flow-system, resulting in a flow-through optosensor (Fig. 5). Flow-injection analysis (FIA) [17,28], sequential-injection analysis (SIA) [29], multi-syringe flow-injection analysis (MSFIA) [30], bead-injection spectroscopy (BIS) [31], and multi-commutation [32] are techniques usually employed for performing this on-line procedure. In comparison with batch methodologies, most flow-through optosensors allow the on-line regeneration of the solid-support and, therefore, they can be reused in successive determinations, saving supplies and experimental time.

Fluoranthene MIPs based on iodinated monomers were used for phosphorescence sensing of fluoranthene in water [33]. Sainz Gonzalo *et al* developed a MIP optosensor for xylenes and TEXs (toluene, ethylbenzene and xylenes) screening [34,35]. Based on the different kinetics of sorption/desorption of carbendazim, carbofuran, and benomyl when interacting with C_{18} silica gel as support, a continuous-flow fluorescence optosensor was developed for their determination in spiked environmental water samples. The method involves a previous separation of the analytes on a minicolumn, placed just before the sensor and packed with the same solid support as the flow-through cell [36]. Following a similar concept of sorption/desorption kinetics, a multi-commutation fluorescence optosensor analysis for fuberidazole and *o*-phenylphenol was performed in well and river water samples [37]. Piccirilli and Escandar developed and applied for first time powdered nylon as support for the implementation of both flow-through fluorescence [38] and phosphorescence [39] sensors of the fungicide thiabendazole in natural waters. Photochemically induced fluorescence was applied for the development of optosensors for the determination of imidacloprid [40], metsulfuron methyl [41], linuron [42] and thiabendazole and metsulfuron methyl [43] in environmental waters. 1-Naphthaleneacetic acid was investigated in water through a flow-through fluorescence sensor [44], and the same research group analyzed 2-naphthoxyacetic acid through both fluorescence and phosphorescence optosensors [45]. Tetracycline, oxytetracycline, chlortetracycline and doxycycline were detected in water using a phosphorescence flow-through optosensor and amberlite XAD-4 as solid support [46]. Recently, tetracycline was also determined using a fluorescence flow-through optosensor based on sephadex G-50 [47].

2.2 Reagent-Mediated Measurement

When an analyte does not have native luminescence properties, sensing can be achieved by monitoring the optical signal of an auxiliar reagent (fluorophore, dye, enzyme, etc), whose response is modulated by the presence of the analyte. The reagent is generally immobilized (by adsorption, covalent bond, ionic attachment or encapsulated) in a matrix which is permeable to the analyte. The matrix can be a thin polymer membrane, controlled-pore glass or microbeads [9,48]. Many of the configurations discussed in Section 2.1 can be implemented in reagent-mediated sensors.

Table 1. Luminescence sensors/probes for inorganic species in water samples

Analyte	**Signal**	**Method**	**Remark**	**LOD**	**Sample**	**Ref**
Cu (II)	RET	Disposable sensor	TP/Zincon/PVC matrix	3.9×10^{-8} M 2.5 ppb	River, well, spring, swimming pool water	[63]
	QF	Probe	LY immobilised on AE particles	1×10^{-8} M, 0.63 ppb	Tap water	[49]
Al(III) and Be(II)	F	BIS-FIA	Sephadex QAE A-25/morin	0.024 ppb Al(III), 10 ppb Be(II)	Tap and river water	[50]
V(V)	F	BIS-FIA	Sephadex QAE A-25/Alizarin Red S	0.450 ppb	Tap and well water	[51]
Hg(II)	F	FIA and batch	Rhodamine B derivative in PVC membrane	8.3×10^{-11} M	Pond water	[52]
	QF	OM, probe	L/PVC membrane/ KTpClPB		Well water	[53]
	QF	OM, flow-cell	H2tpp/PVC membrane	4.0×10^{-8} M	Tap water	[54]
	QF	OM, flow-cell	Porphyrin/PVC membrane	8.0×10^{-9} M	River, tap, waste water	[55]
	QF	OM, flow-cell-bifurcated OF	H_3(tpfc)/PVC membrane		River and tap water	[56]
	QF	OM, flow-cell-bifurcated OF, HCl (R)	DTPP/PVC membrane		River water, industrial wastewater	[57]
	QF	OM, probe	EHT/PVC membrane	1.8×10^{-10} M, 36 ppb	Tap water	[58]

Table 1. (*continued*)

	F	Syringe procedure, probe	Rhodamine 6G derivative and nylon membrane	0.4 ppb	Mineral, underground river water	[64]
	QF	Probe, EDTA (R)	Mesoporous silica /1,8-naphthalimide	200 ppb	Drinking, seawater	[65]
	QF	Probe	Hacid/LDH film *via* EPD method	6.3×10^{-8} M	Spiked, tap, lake water	[66]
	F	Probe	Rhodamine 6G/ QDs-silica NPs	0.520 ppb, 2.59×10^{-9} M	Tap, river water	[76]
	SF	Probe	MPA stabilized CdTe/ dOB/QDs	4.2×10^{-9} M	Tap, lake water	[81]
Hg(II) and Cu(II)	PLQ	Probe, GSH (R)	QDs-multilayer films	Lineal range: $(0.05\text{-}5)\times10^{-7}$ M for Hg^{2+}, $(0.01\text{-}1)\times10^{-6}$ M for Cu^{2+}	Artificial water sample	[82]
Zn(II)	QF	Probe, EDTA (R)	MCB/PVC membrane	2.5×10^{-8} M, 1.6 ppb	Tap water	[59]
Ni(II)	QF	Probe, EDTA (R)	PVC/KTpClPB/TTBB		Wastewater	[60]
Pb(II)	F	Probe, HCl-thiourea (R)	Triazolo-thiadiazin derivative/PVC	2.2×10^{-8} M	Tap and river water	[61]
	QF	Probe, dithiotritol (R)	Fluoroionophore L2/ PVC/ KTpClPB	2.0×10^{-7} M	Tap water	[62]
Be(II)	QF	Probe, F^- (R)	Beryllon II/MgAl-LDH	4.2×10^{-9} M	Lake and tap water	[67]
CN^-	Increase of F with Cu(II)	Probe	Boronic acid-linked hydrazide/fluorescein encapsulated in AMP/Gd^{3+}CNPs	20×10^{-6} M (naked-eye) 4.03×10^{-6} M (instrumental)	Drinking water	[68]
Cr(VI)	IFE	Probe	Luminescence NPs ($NaYF_4$:Yb^{3+}, Er^{3+})	2.4×10^{-8} M	Tap, river and waste water	[69]
Cd(II)	PL in NIR	Probe	CdTe/CdS QDs	Lineal range: $(0.1\text{-}2)\times10^{-6}$ M	Tap and river water	[80]
As(III)	QF	SIA	AsH_3 diffused across PTFE membrane and interacted with CdS-MAA QDs	70 ppb	Ground water	[83]
Cu(II) and CN^-	Cu^{2+}: QF; CN^-: F	FIA, EDTA (R for Cu^{2+}), Cu(II) (R for CN^-)	Imidazole microspheres/functionalized CPs	Cu(II): 1 ppb CN^-: 8 ppb	Tap and mineral water	[86]
Ag(I)	F	Distal OF bundle	PVC microspheres onto the distal end of an OF bundle		Pond water	[89]

Table 1. (*continued*)

Abbreviations (other are defined in the text): AE, anion exchange; AMP/Gd^{3+} CNPs: nucleotide/lanthanide coordination nanoparticles; Beryllon II, 2-(3,6-disulfo-8-hydroxynaphthylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate; CPs, conjugated polymers; DFC, diphenylcarbazone; dOB, chemically denatured ovalbumin; DTPP, 5-*p*-[[4-(10'-15',20'triphenyl-5'-porphinato)phenyloxyl]-1-butyloxyl]-phenyl-10,15,20 triphenylporphine; EDTA, ethylenediaminetetraacetic acid; EHT, 4-ethyl- 5-hydroxy-5,6-di-pyridin-2-yl-4,5-dihydro-2H-[1,2,4]triazine-3-thione; EPD: electrophoretic deposition method; F, fluorescence; GSH, glutathione; Hacid, 1-amino-8-naphthol-3,6-disulfonic acid; H2tpp, 5,10,15,20-tetraphenylporphyrin; H_3(tpfc), 5,10,15-tris(pentafluorophenyl) corrole; KTpClPB: potassium tetrakis(*p*-chlorophenyl) borate; IFE: inner filter effect; LDH, layered double hydroxide; LY: Lucifer yellow; L, 1-(dansylamidopropyl)-1-aza-4,10-dithia-7-oxacyclododecane; L2, (5,8-bis((5'-chloro-8'-hydroxy-7'-quinolinyl) methyl)-2,11-dithia-5,8-diaza-2,6-pyridinophane); LOD, limit of detection; MAA, mercaptoacetic acid; MCB, 1-methyl-1-phenyl-3-[1-hydroxyimino-2-(succinimido)ethyl] cyclobutane; morin: 2',3,4',5,7-pentahydroxyflavone; NIR, near infrared; NPs, nanoparticles; OF, optical fiber; OM, optode membrane; MPA, 3-mercaptopropionic acid; PL, photoluminescence; QF, quenching of fluorescence; QPL, quenching of photoluminescence; R, regenerating reagent; RET, radiationless resonance energy transfer; SIA, sequential injection analysis; TP, porphyrazine 2,7,12,17-tetra-*tert*-butyl-5,10,15,20-tetraaza-21H,23H-porphine; TTBB, 2,5-thiophenylbis(5-*tert*-butyl-1,3-benzexazole).

This approach is widely used for the construction of probes and sensors devoted to determine metal cations and anions, which are not naturally fluorescent, through the signals produced by their interaction with auxiliary reagents. Table 1 summarizes reviewed works involving probes and sensors for ionic compounds found in environmental waters.

Different fluorophors (lucifer yellow, morin, alizarin red S) immobilized in ionic exchanger particles were used to determine Cu(II) [49], Al(III) and Be(II) [50] and V(V) [51]. Based on either the enhancement or quenching of fluorescence, polyvinyl chloride (PVC) membranes containing several organic molecules have been used to determine Hg(II) [52-58], Zn(II) [59], Ni(II) [60], Pb(II) [61,62], and Cu(II) [63] in natural waters.

A PVC membrane probe based on a Rhodamine B derivative (RND) was recently described for the determination of Hg(II) ion in environmental water samples and fish [52]. The method was developed in batch and also in a flow-system. For bulk measurements, RND-PVC-coated glass slides were placed in diagonal positions into a standard quartz cell, which was filled with a sample solution. The flow-through cell consisted of two separate teflon blocks, an optical glass window, a sample chamber containing the sensing membrane coated on the glass slide, a silicon gasket and screws for clamping the blocks, as is shown in Fig. 6. The measuring cell was mounted in the spectrofluorimeter and connected with a peristaltic pump. In this case, the conditioning, measurement and regeneration steps were implemented by passing carrier, Hg(II) ion and regenerating solutions, respectively, through the flow cell. In both batch and flow-through configurations the emission was detected at a 90° angle relative to the incident light.

The viability of determining Hg(II) ion residues in real water samples was demonstrated through a probe based on the mercury-promoted ring opening of the spirolactam moiety of a rhodamine 6G spirocyclic phenylthiosemicarbazide derivative retained in commercial nylon membranes [64].

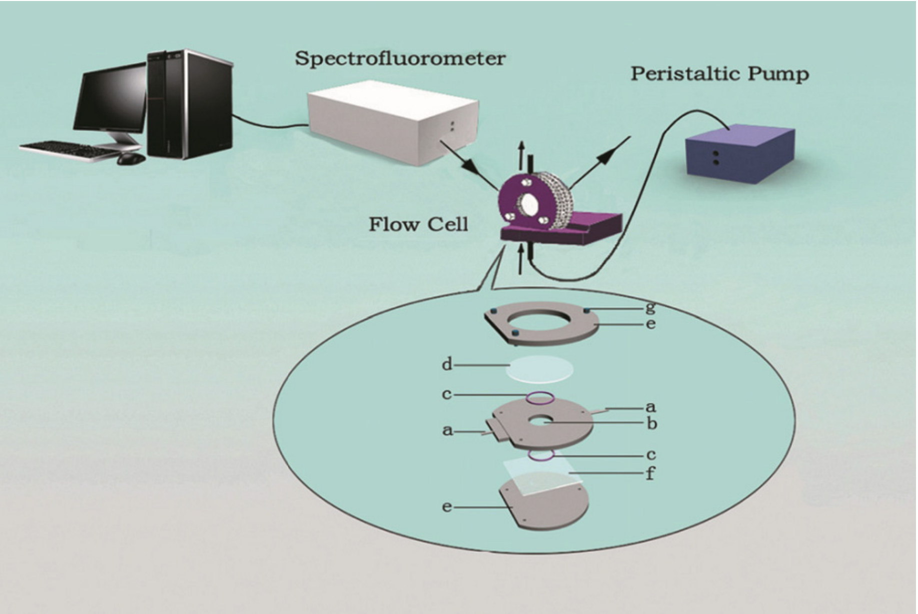

Fig. 6. Schematic diagram of the flow-through cell: (a) Teflon tube for sample in and out; (b) sample chamber; (c) gasket; (d) optical glass window; (e) Teflon cover; (f) sensing membrane coated on the glass slide; (g) fixing screws. (Reprinted with permission from [52]. Copyright 2012 Elsevier).

For monitoring Hg(II) in domestic and sea waters through fluorescence quenching, Meng *et al* developed an hybrid mesoporous silica functionalized with 1,8 naphtalimide-base receptor [65], and Sun *et al* obtained a layered double hydroxide film with intercalated 1-amino-8-naphthol-3,6-disulfonic acid *via* an electrophoretic deposition method [66]. The assembly of Beryllon II and MgAl–layered double hydroxide (LDH) nanosheets on quartz using the layer-by-layer deposition technique was used to quantify Be(II) in lake and tape water [67]. Kulchat *et al* proposed a method to determine CN^- in presence of Cu^{2+} based on a sensor molecule, containing boronic acid-linked hydrazide and fluorescein moieties. This molecule was encapsulated in nucleotide/lanthanide coordination nanoparticles to avoid hydrolysis in water [68]. The inner filter effect of luminescent nanoparticles ($NaYF_4$:Yb^{3+}, Er^{3+}) produced by the Cr(III)-diphenylcarbazone complex was exploited to assess Cr(VI) in tap, river and waste waters [69]. Azab *et al* developed a fluorescent sensing tool for screening primary aliphatic amines in water and soil samples [70]. This sensor is based on a pyrilum dye embedded into a polymeric cocktail, which is deposited on the bottom of wells in microtiter plates.

Because of their superior optical properties, quatum dots (QDs) are increasingly employed for sensing purposes [71,72]. Wang *et al* determined phosphorimetrically pentachlorophenol using surface molecular imprinting on Mn-doped ZnS QDs [73]. Stringer *et al* quantified 2,4 dinitrotoluene and 2,4,6-trinitrotoluene through fluorescence quenching of QD labeled microparticles [74]. The latter compound also was determined through the phosphorescence quenching of Mn-doped ZnS QDs [75]. The enhancement of emission signal of rhodamine 6G grafted on silica nanoparticles-QDs was proposed to determine Hg(II) [76]. A low limit of detection (2.4×10^{-12} M) was achieved in the determination of 1,4–dihydroxybenzene using the fluorescence resonance energy quenching of mercaptosuccinic acid–capped CdTe QDs immobilized on silica particles [77]. Fullerene in spiked river water was analyzed using CdSe/ZnS QDs coated by *p-ter*butylcalix[8]arene. The method allows the detection of 5 μg L^{-1} of fullerene in a simple and fast way [78]. QDs-MIP composite nanospheres were successfully applied to direct fluorescence quantification of the organophosphate insecticide diazinon in water. This method selectively detects down to 50 ng mL^{-1} of diazinon and it provides a strategy to obtain inorganic-organic nanocomposites with potential applications in environmental analysis [79]. Cd(II) and Hg(II) were quantified in diverse types of waters (tap, river, lake) using CdTe/CdS [80] and CdTe-chemically denatured ovalbumin QDs [81], respectively. In addition, Hg (II) and Cu(II) were quantified by fluorescence quenching of QD-multilayer films [82]. Butwong *et al* proposed a method to quantify arsenic in ground water which consists in the measurement of the fluorescence quenching of mercaptoacetic-acid capped CdS QDs after on-line arsine generation with BH_4Na and HCl through a SIA system [83].

The so-called “sol-gel” process is a technique widely used for the production of materials, starting from a colloidal solution that acts as the precursor (e.g. metal alkoxides) which undergoes hydrolysis and polycondensation reactions to produce a porous matrix in which the reagent is encapsulated and into which the analyte molecules can diffuse. Materials obtained from this process have outstanding mechanical and thermal stability and good optical characteristics and, therefore, are very suitable for the development of optical sensors [84]. A sol-gel technique was applied to develop luminescent Eu(II) transparent films deposited on glass slides, in order to obtain sensor devices capable of monitoring transition metal ions in aqueous solution [85]. Álvarez Diaz *et al* proposed an optosensor based on imidazole-functionalized colpolymer microspheres, obtained by a sol-gel method, to quantify Cu(II) and cyanide ion [86]. A sol-gel membrane modified with 2-hydroxy-1-naphthaldehydene-8-aminoquinoline was developed as a model for detecting Pb(II) [87].Trace levels of anthracene, phenanthrene and pyrene were detected in tap and mineral water through the enhancement of fluorescence of hydrophilic QDs (modified CdSe/ZnS) entrapped into sol-gel membranes [88].

3 Fiber-Optic Sensor Platforms

Optical fibers are usually employed as platforms in optical sensors, especially because they allow optical spectroscopy to be performed on sites inaccessible to conventional spectroscopy. McDonagh *et al* [2] summarized common configurations used for fiber-optic platforms (Fig. 7). In turn, fibers can only act to transport the optical signal to and from the sensing environment (passive fiber-optic system) or be doped with a selective indicator, having thus an active participation in the detection (active fiber-optic system). In the first case, the intrinsic optical property of the analyte (e.g. fluorescence emission) is measured. In the second one, the signal of an immobilized indicator is monitored.

3.1 Passive Fiber-Optic System

A typical picture of a passive fiber-optic fluorescence sensor comprises a sensitive material that fluoresces upon interaction with the analyte of interest and a fiber bundle (as shown in Fig. 7d). In the fiber bundle, the central fiber delivers the excitation light to the external sensor element and the outer fibers are used to collect and transport the emitted fluorescence to a suitable detector.

A fluorescent optical microsensor array for rapid sensing of trace levels of Ag^+ in pond water was fabricated using plasticized PVC-based fluorescent microspheres deposited onto the etched distal end of an optical fiber bundle [89].

The bifurcated fiber bundle can be used to deliver excitation light with one fiber and to collect the excited fluorescence with the second. This latter configuration has been used for the fluorescence-based detection of 2,6-dinitrophenol (A selective optical chemical sensor for 2,6-dinitrophenol based on fluorescence quenching of a novel functional polymer). Bifurcated fibers were also employed to quantify Hg(II) ion through fluorescence quenching [56,57].

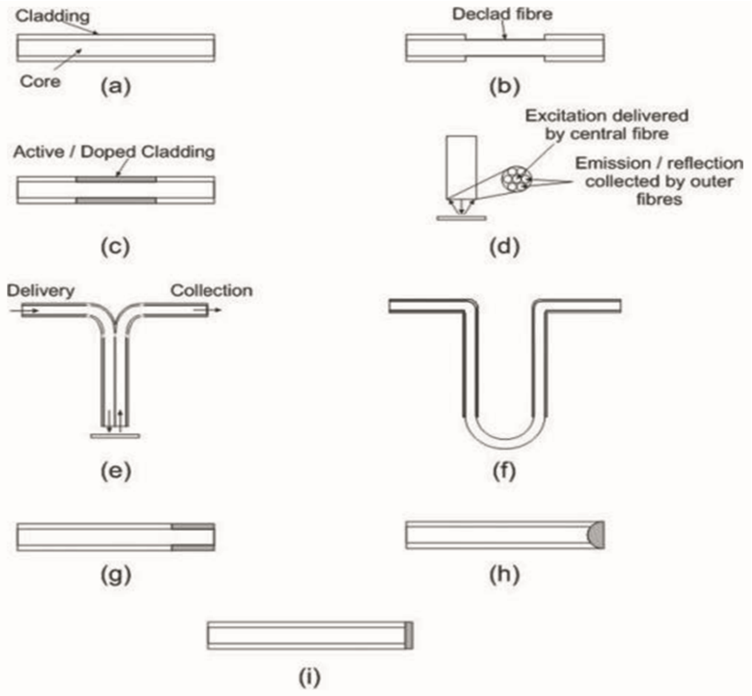

Fig. 7. Configurations for fiber-optical chemical sensors: (a) unmodified; (b) declad; (c) active or doped cladding; (d) fiber bundle; (e) bifurcated fiber bundle; (f) U-bend (shown declad); (g) tip with active cladding; (h) etched tip; (i) modified end-face. (Reprinted with permission from [2]. Copyright 2008 American Chemical Society).

A MIP using Al(III) ion as the template molecule and 8-hydroxyquinoline sulfonic acid as the the ligand to form a fluorescence complex was characterised for the implementation of an optosensor for this metal ion [90]. A self-designed flow-cell included a glass tube filled with the MIP fitted into a black box (to avoid interference from stray light) and a fibre optic cable attached at the top of the box.

3.2 Active Fiber-Optic System

In reagent-based optical sensor systems, fluorescent indicator molecules are added to the fiber platform. In most active systems, the sensor material is included in a solid matrix in the form of a monolith or a thin film. The matrix encapsulates the reagent such that it is accessible to the analyte. In their review, McDonagh *et al* give a detailed explanation of the different configurations which can be achieved in these types of sensors [2].

Two commonly used immobilization matrices are polymeric and sol-gel materials. The most widely used polymers are polystyrene (PS), polyvinyl chloride (PVC), polymethyl methacrylate (PMMA), polydimethyl siloxanes (PDMS), and polytetrafluoroethylenes (PTFE) and ethyl cellulose. Besides, sol-gel materials are very adequate to be coupled to a fiber-optic system. The process can be controlled in order to obtain materials of desired porosity and polarity [91]. The auxiliary reagent can be either entrapped or covalently bounded to the sol-gel matrix. Fiber-optic sensors based on sol-gel films have been intensely explored as pH, gas, ionic species and solvent sensors [84].

Lieberzeit *et al* highlighted some features that imprinting offers for sensor design and showed the ability and variability of this technological platform for the detection of PAHs (naphthalene and pyrene) among other compounds [92].

The chemical agents EA2192, VX, sarín and soman were determined at part-per-trillon levels in multiple water matrices using lanthanide-sensitized luminescence and MIP containing europium polymerized onto a fiber-optic [93]. A plasticized PVC–curcumin moiety membrane was used in a bifurcated optical fiber based flow-optosensor for the determination of 2,6-dinitrophenol through fluorescence quenching measurements [94]. Employing similar bifurcated optical fiber systems but different supports (β-CD polymer and pyrene/dimethyl-β-CD complex immobilized in plasticized PVC membranes), the same authors determined bisphenol A through fluorescence [95] and fluorescence quenching [96] signals, respectively.

4 Strategies of Evaluation Involving Multivariate-Chemometric Calibration

Because of the complexity of environmental samples, luminescence optonsensors, like most of sensors based on spectroscopic properties, suffer lack of selectivity due to the probability that similar compounds show similar luminescence properties. A current strategy for resolving the spectral overlapping in complex environmental matrices and, thus, ensuring interference-free quantitation is the coupling to multivariate calibration methods [97]. Specifically useful are second-order calibration methods which achieve the so called 'second-order advantage'. These methods allow the quantitation of analytes even in the presence of unexpected sample components [98].

The simultaneous determination of the systemic fungicides carbendazim and thiabendazole in natural waters was achieved using fluorescence excitation-emission matrices obtained after the extraction of the analytes over a C18-membrane surface [99]. The applied algorithm, partial least-squares with residual bilinearization (PLS/RBL), was capable of both correctly predicting the concentration of the studied compounds in the presence of unsuspected species and overcoming the inner-filter effect. Valero Navarro *et al* determined two naphthylamines in drinking waters coupling second-order calibration to a MIP-fluorescence optosensing system [100]. Using a flow-through optosensor based on C18-bonded phase and second-order algorithms, thiabendazole and fuberidazole where quantified in the presence of carbaryl, carbendazim and 1-naphthylacetic acid [101]. A flow-through spectrofluorimetric sensor, also based on C18-bonded phase as substrate in the flow cell and a first-order calibration approach, was proposed for the resolution α-naphthol, o-phenylphenol and thiabendazole in environmental water samples [102]. First derivative emission spectra of the analytes recorded during the process of retention-elution were used to provide multivariate data which were processed with the partial least-squares (PLS) algorithm. Benzo[*a*]pyrene and dibenz[*a,h*]anthracene were fluorimetrically determined in the presence of the remaining EPA-PAH priority pollutants using a probe based on nylon membranes and second-order calibration as strategy of evaluation [103]. The same research group determined six heavy-PAHs in the presence of another 10 interfering PAHs, applying second-order multivariate calibration to the data obtained with a flow-through optosensor (sensor phase: silica gel C18) interfaced to a fast-scanning spectrofluorimeter [104]. Very recently, microporous nylon membrane was employed as a fluorimetric probe for the quantification of the herbicide bentazone in natural waters. Second-order calibration using parallel factor analysis (PARAFAC) allowed the determination at low levels in a highly interfering medium [105].

5 Conclusions

Chemical sensors based on luminescence signals are relevant in environmental measurements due to their multiple advantages, highlighting their high sensitivity and usefulness for the determination of contaminants at very low concentrations. Fortunately, most optosensors are compatible with green-chemistry principles, and this quality makes them even more attractive. Bulky sensors are being gradually replaced by miniaturized devices, and flow methodologies are preferable than those carried out in batch. However, independently of their final configurations, new approaches for the development of novel probes and sensors for the determination of contaminants in the environment are continuously reported.

Acknowledgments. Universidad Nacional de Rosario and CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas, Project PIP 1950) are gratefully acknowledged for financial support.

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