Recent Trends in Monitoring of European Water Framework Directive Priority Substances Using Micro-Sensors: A 2007-2009 Review

P. Namour, M. Lepot, N. Jaffrezic Renaud

To cite this version:

P. Namour, M. Lepot, N. Jaffrezic Renaud. Recent Trends in Monitoring of European Water Framework Directive Priority Substances Using Micro-Sensors: A 2007-2009 Review. Sensors, 2010, 10, p. 7947 - p. 7978. 10.3390/s100907947. hal-00536853

HAL Id: hal-00536853
https://hal.science/hal-00536853
Submitted on 17 Nov 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Abstract: This review discusses from a critical perspective the development of new sensors for the measurement of priority pollutants targeted in the E.U. Water Framework Directive. Significant advances are reported in the paper and their advantages and limitations are also discussed. Future perspectives in this area are also pointed out in the conclusions. This review covers publications appeared since December 2006 (the publication date of the Swift report). Among priority substances, sensors for monitoring the four WFD metals represent 81% of published papers. None of analyzed publications present a micro-sensor totally validated in laboratory, ready for tests under real conditions in the field. The researches are mainly focused on the sensing part of the micro-sensors. Nevertheless, the main factor limiting micro-sensor applications in the environment is the ruggedness of the receptor towards environmental conditions. This point constitutes the first technological obstacle to be overcome for any long-term field tests.

Keywords: sensors; water framework directive; metals; priority substance
1. Introduction

The Water Framework Directive (WFD) governs European water policy. WFD has been in place as the main European regulation for the protection of water resources and the water environment since 2000 [1]. One of its principal objectives is to achieve good chemical and ecological status and to restore water bodies to a ‘good status’ by 2015. WFD requires management of water bodies so that the water quality does not affect their ecological services. Chemical status refers to specific pollutants (e.g., priority substances or priority hazardous substances) for which environmental quality standards (EQS) are proposed and defined for pollutants as minimum requirements [2].

As the WFD implementation gradually comes into effect in European countries, the environmental metrology market is bound to increase over the coming years. In view of the high cost of the laboratory analyses required and the potential artifacts that may be introduced during the conventional sampling protocol: “send a technician, take an isolated sample, send it to the laboratory and analyze it” with at best, in conventional water chemistry, a 24-hours flow proportional composite sample, a new type of field analysis must be designed. An average sample obscures the essentially dynamic character of a polluting event and average contents are devoid of any ecological realism. Biocenoses in rivers are never exposed to average contents, which have no actual existence as far as they are concerned. They are in reality exposed to changes in their physicochemical ambience. A first monitoring of dissolved copper, lead and cadmium with a submersible voltametric flow cell for periods of four days in coastal waters shows that the potentially most toxic forms of metals may vary in concentration on a time scale of less than one hour [3]. This first data confirm the poor ecological relevance of the conventional sampling protocol and the necessity of a continuous measurement. The greater and more sudden these changes, the more disturbance they cause. In terms of toxicology, fluctuation is a more important parameter than the average level, and in the present case the concentration peak reached by the pollutant is more important than the average concentration. The ecological pertinence of such a procedure is more than problematic [4]. New environmental monitoring strategies must be designed. A possible avenue that merits further exploration involves the deployment of low-cost instrumentation allowing massive data logging, as well as tools for subsequent data validation, management and interpretation. However, while this new type of instrumentation is possible, and even desirable, such deployment cannot at the present time cover all the WFD’s parameters and there is little probability of this situation changing before 2015, or even 2021. Consequently, faced with the magnitude of this metrological challenge and the urgency of the situation, a paradigm shift is required in order to imagine a new approach to the problem of water monitoring. Given this situation, current research on micro-sensors is leading to the emergence of many measuring principles. The Swift report (http://www.swift-wfd.com), published in December 2006, lists a wide range of monitoring methods currently available or under development for supporting the WFD. This review covers publications after December 2006, the publication date of the Swift report. It then covers the period extending from January, 2007 to December 2009, and concerns micro-sensors of so called priority substances from the list quoted in appendix II of the Common Decision n°3/2008 of December 20th, 2007 [6]. This review, although not being able to aspire to the exhaustiveness, constitutes a relatively exact panorama of the recent research efforts in the field of the measurement of priority substances in the water using micro-sensors.
For practical reasons, with the analyte constituting the access key for chemical analysts, micro-sensors were firstly classified according to the measured analyte and then, for one analyte, according to the measurement principle or transduction mode: electrochemical and optical. The papers will then be presented according to the following classification: first the measured analyte then, when several technologies are used, they were grouped by type. Finally we tried to focus this review mainly on the micro-sensors at the field validation stage, that is the systems having passed lab tests and susceptible to field validation. The criteria of publication analysis are: the type of aquatic environment studied, the detection limit and the reproducibility.

Finally, with a concern for sustainable development and the eco-design of instruments installed in natural environment, this review does not take into account publications presenting methods involving toxic compounds, such as “heavy metals”, in particular mercury impregnation or films, even if the quantities used are relatively low. Indeed, substances such as cadmium or mercury have been classified as ‘priority hazardous substances’ in the Decision n°2455/2001/EC [5] and Directive 2008/32/CE [6], for which Member States should implement necessary measures with the aim of ceasing or phasing out emissions, discharges and losses into water of those priority hazardous substances which derive from human activities. So it is preferable to banish these hazardous substances from our devices, rather than quibble over low or negligible implemented quantities, and to be vigilant about the potential toxicity of any new substances used in our devices.

Furthermore, development of new devices using priority hazardous substances leads to a commercial dead-end, and a waste of time and money: they cannot be used in Europe, and even in the other parts of the world. Indeed, mercury is recognized as a chemical of global concern. US EPA’s Roadmap for Mercury (5 July 2006) promotes reducing mercury in processes and products, even where cost-effective substitutes do not exist. The overall goal of the Global Mercury Partnership of United Nations Environment Programme (Governing Council Decision 25/5, Nairobi, Kenya, 16–20 February 2009) is to reduce and eventually eliminate mercury use in products and processes, and raising awareness of mercury-free alternatives. Among these products electric and electronic devices are targeted.

2. Reviews & Books

Some recent reviews were published during the years 2007–2009. Johnson et al. [7] refocus problems posed by the punctual sampling of dynamic systems such as rivers. The authors insist on the necessity of high frequency and continuous measures in time, as well as on the obligation of taking into account spatial variations. They also regret the current absence, for the most part, of simple, selective and sensitive enough sensors for the chemical elements of interest to the geochemist operating without drift over long periods. Pejcic et al. [8] surveyed some of the work that has been undertaken using sensors to detect hydrocarbons. Of the various transducers examined in this review the optical-based sensor appears to be the most promising in terms of water monitoring. The Bosch et al. review [9] in the journal Sensors, is about the use of optical fibre micro-biosensors, mainly in biological applications. Let us note a section dedicated to the measurement of metals via cells or immobilized enzymes and micro-biosensors detecting PCB or pesticides via antibodies immobilized on silica fibres. Also let us quote the Lieberzeit and Dickert review [10] dedicated to the
sensors applicable to the environmental chemistry, operational in the field, during these last five years. The authors end their paper with the very scarce literature published on actually operational sensors, albeit with some breakthroughs in the metal measurement domain. The development of simple and strong optical or electrochemical prototypes adapted to the field conditions, will permit one to envisage actual field monitoring in a near future. Clare Reimers’ review [11] is more particularly centred on the usage of glass microelectrodes in oceanography. A section is dedicated to the study of metal speciation in the marine environment with minimal sampling artefacts.

Two articles review the challenges associated with metal speciation studies, and focus on voltammetric techniques for the in situ study of metal speciation. More specifically, they summarize the specific conceptual, analytical, and technical criteria that must be considered to develop rugged, field deployable, non-perturbing sensors and probes [12,13]. Lange et al. [14] overviewed surface acoustic wave-based biosensor technology, and a small section was devoted to atrazine and PAH detection. The review of Moreno-Garrido [15] draws a general picture of the advances in immobilization techniques and biotechnology, using freshwater and marine micro-algae, in environmental aquatic research for the toxicity measurement of substance or effluent. Jones and Compton’s review [16] summarizes works using boron-doped diamond (BDD) electrodes for stripping voltammetry, particularly for measurements of toxic metals such as cadmium or lead. BDD does not seem to be a suitable mercury substitute in all cases, but is one of the more widely applicable alternative electrode materials in comparison to glassy carbon or solid metal electrodes. Jaffrezic-Renault and Dzyadevych [17] presented the application of the conductometric measurement method to environmental monitoring and specifications obtained for the detection of different pesticides, herbicides and heavy metal ions, based on enzyme inhibition.

In a detailed review, Seidel and Niessner [18] described microarray techniques for the simultaneous detection of multiple analytes and presented some environmental applications such as pesticides, toxins and endocrine-disrupting compound detection in water. Recent advances in the development and applications of nucleic acid-based biosensors for environmental application are reviewed by Palchetti and Mascini [19], with special emphasis on functional nucleic acid elements and the detection of chemically-induced DNA damage caused by genotoxic pollutants as some PAH, pesticides or solvents. A chapter of book “Antiterrorism and Homeland Defense: Polymers and Materials” is devoted to porphyrin-enzyme complexes for the detection of organophosphates using evanescent wave absorbance spectroscopy (EWAS) [20]. Nolan and Lippard [21] provided a very comprehensive account of progress in the design and application of optical sensors for mercury, in the environmental and biological media, up until July 2007.

Diamond et al. [22] present the concept of ‘wireless sensor networks’. A part of their review is dedicated to remote environmental monitoring and highlights limitations with the current manifestations of these platforms, particularly with respect to integration of chemo-/biosensing capabilities. In the same way, Strobl and Robillard [23] give insight into the strategies of water quality monitoring network design for surface freshwaters, along with their weaknesses and shortcomings. They propose nine recommendations for the successful development of a methodology for designing monitoring networks. A section of Bogues’ article [24] gives a brief overview of the environmental sensing technologies in water quality monitoring and considers briefly the research effort.
Jaffrezic-Renault [25] presents in *Actualité Chimique* different kinds of electrochemical micro-sensors allowing the *in situ* monitoring of pollutants in waters: heavy metals, ammonium, total organic carbon, organophosphate pesticides. The review of Baruah and Dutta [26] on nanotechnology applications in pollution sensing in agriculture and environment contains an important section on the measurement of pollutants by means of nano-structured materials. This review is far from exhaustive concerning the topic of micro-sensors and certain references are more than 10 years old. Pesavento *et al.* [27] presented the electrochemical methods for metal speciation in natural waters, mainly by means of voltammetry. It is noteworthy that a section is dedicated to *in situ* measurements, especially focused on practical needs. The single micro-sensor presented is a gel electrode containing mercury. The second part of this review deals with alternative procedures as separation techniques based on ion exchange and complexing resins, and micro separation methods as Donnan membrane technique, diffusive gradients in thin-film gels and permeation liquid membrane. Reardon *et al.*’s review [28] focuses on photoluminescence-based biosensors of potential use in the environmental applications. They give examples of optical biosensors for organics (aromatic solvents, PAH, organophosphate or halogenated pesticides) and metal determinations (Hg, Cd, Pb and Ni), however these references are previous to 2007. Leray and Value [29], after a summary of the main classes of fluorescence molecular receptors for the detection of toxic metal ions (Photoinduced Electron or Charge Transfer, Excimer Formation or Disappearance and Energy Transfer), present different calixarene-based fluoroionophores for the detection of caesium, mercury, lead and cadmium. A review of Selid *et al.* [30] examines different useful micro- and nano-sensors for mercury determination, mainly in healthcare and in a lesser extent, in the environmental field. Finally, David *et al.* [31] published a review on alkylphenols in marine and coastal environment, mainly centred on the environment contamination, however a section is dedicated to their detection in environmental matrices by biological tests on cells but not strictly involving micro-sensors as we understand them.

3. Scientific Articles

3.1. Metals

The WFD targets four priority metals: cadmium, mercury, nickel and lead [1]. Table 1 summarizes the various target values for freshwater water bodies. The strongest constraints are given by the SEQ-Eau, a water quality evaluation system developed by French Water Agencies in order to maintain the water biological balances in an optimal way. The detection limits of micro-sensors should be equal or lower than SEQ-Eau target values, although they do not represent statutory values, as the limit values of the Order 2001-1220 are only imperative for drinking water.

The analysis of the publications from 2007 to 2009 in the field of micro-sensors, shows that research efforts mainly concern the determination of WFD metals in waters (126 papers), the detection of WFD organic substances being the subject of less attention (24 papers), then 83% of the papers concern only 17% of priority substances. The sensors for metal detection divide up roughly equally between electrochemical (56%) and optical (44%) techniques, with strong disparities according to the metal concerned. As a general rule the electrochemical methods are preferred for the detection in water
of cadmium (86%), nickel (67%) and lead (86%). On the other hand optical methods are proposed for mercury detection in 73% of the papers.

**Table 1.** Summary of the superior limit concentrations ($\mu$g/L) of metallic elements, recommended or statutory in fresh water.

|                | Surface water (good chemical status) | Drinking water          |
|----------------|--------------------------------------|-------------------------|
|                | WFD [2]                              | AA-EQS                  |
|                | INERIS** PNEC [32]                   | SEQ-Eau                 |
|                | Order in Council 2001-1220 [33]      | SEQ Underground water   |
| Cd             | 0.08–0.25                            | 0.21                    |
|                |                                      | 0.001                   |
|                |                                      | 5                       |
|                |                                      | 1                       |
| Hg             | 0.05                                 | 0.24                    |
|                |                                      | 0.007                   |
|                |                                      | 1                       |
|                |                                      | 0.5                     |
| Ni             | 20                                   | 0.5                     |
|                |                                      | 0.25                    |
|                |                                      | 20                      |
|                |                                      | 10                      |
| Pb             | 7.2                                  | 5                       |
|                |                                      | 0.21                    |
|                |                                      | 10                      |
|                |                                      | 5                       |

*AA-EQS: Environmental quality standards expressed as an annual average value; **INERIS values are PNEC (Previsible Non Effect Concentration) from the following reports: Cd [29]; Hg [30]; Ni [31]; Pb [32]. SEQ-Eau: Système d'Evaluation de la Qualité de l'eau (water quality evaluation system) developed by the French Water Agencies.

Approximately twenty articles deal with the continuous determination of cadmium in water, mainly (81%) by electrochemical techniques (Table 2). Only five articles about optical techniques for cadmium determination were published from 2007 to 2009 (Table 3).

**Table 2.** Analytical characteristics of electrochemical sensors for cadmium determination in water, published between 2007 and 2009.

| Method                                                  | Tested sample                  | LoD (μg/L) | RSD (%) | Ref.   |
|---------------------------------------------------------|--------------------------------|------------|---------|--------|
| DPASV on multiwalled carbon nanotubes/Bi film modified glassy carbon | Tap, river & spring waters     | 0.2        | 4.6     | [34]   |
| DPASV on boron-doped diamond                            | Acetate buffer                 | 0.4        | nr      | [35]   |
| DPASV on bismuth film/graphite electrode                | Acetate pH 4                   | 0.5        | nr      | [36]   |
| SWASV on hydroxyapatite modified carbon paste electrode | Tap water                      | 0.5        | 3.8     | [37]   |
| Inhibition of urease immobilized on screen-printed 10% rhodinized carbon electrode | Standards                      | 0.6        | nr      | [38]   |
| DPASV on bismuth/poly(p-aminobenzene sulfonic acid) film electrode | Tap water                      | 0.6        | 3.4     | [39]   |
| SWASV on antimony film carbon paste electrode           | Spiked lake water              | 0.8        | 3.8     | [40]   |
| DPASV on multiwalled carbon nanotubes-sodium dodecyl benzene sulfonate modified stannum film electrode | Tap water                      | 0.9        | 4.5     | [41]   |
| Conductometric measurement of alkaline phosphatase activity of the microalgae Chlorella vulgaris on two gold interdigitated electrodes | Wastewater                     | 1.0        | nr      | [42]   |
Table 2. Cont.

| Method                                  | Electrolyte                    | pH   | RSD  | LoD   |
|-----------------------------------------|--------------------------------|------|------|-------|
| SWASV on bismuth-film electrode         | River water                    | 1.0  | 4.4  | [43]  |
| LASV on a zeolite NH4-Y modified carbon paste electrode | Ground & wastewaters           | 1.0  | 7    | [44]  |
| SWASV on polymer-modified glassy carbon electrode | Plating wastewater            | 1.0  | 2.5  | [45]  |
| Conductometric measurement of alkaline phosphatase activity of the microalgae *Chlorella vulgaris* on two platinum interdigitated electrodes | Tris-HCl buffer                | 1.0  | 7    | [46, 47] |
| SWASV on square array of 8 × 8 screen-printed carbon-based microelectrodes | River                           | 1.3  | 18   | [48]  |
| DPASV on glassy carbon electrode modified with a thiacalix[4]arene film | River & lake waters            | 2.2  | 3.2  | [49]  |
| SWASV on bismuth nanoparticle modified boron doped diamond | Standard pH 1.2                 | 2.3  | nr   | [50]  |
| SWASV on glassy-carbon electrodes functionalized with composite of Nafion and thiol self-assembled monolayers on mesoporous supports | River water & seawater         | 2.5  | 5    | [51]  |
| SWASV on screen-printed graphite electrode | Seawater                       | 2.9  | 2.3  | [52]  |
| Cyclic voltammetry of invertase-glucose oxidase activities on platinum microelectrode | Phosphate buffer               | 3.0  | nr   | [53]  |
| SWASV on carbon disk screen-printed electrode with Bi ions | Wastewaters Spiked tap water   | 3.6  | 10   | [54]  |
| SWASV on nitrogen doped diamond-like carbon microelectrode array | Acetate pH 4                   | 4.6  | nr   | [36]  |
| DPASV on screen printed carbon electrode | Mine water                     | 9    | 4.5  | [55]  |
| ASV on bismuth electrode                | Pore & ground water            | 9.3  | 2    | [56]  |
| ASV on screen-printed bismuth oxide/graphite electrode | Wastewater                     | 16   | 9.1  | [57]  |
| DPASV on tape ion sensor based on metal ion transfer reactions at the water/gel micro-interface | Standards                     | 20   | nr   | [58]  |
| LSASV on antimony nanoparticle modified boron doped diamond | Standard pH 1                  | 38   | nr   | [59]  |
| Potentiometry on ion-selective electrodes with PVC/4-hydroxy salophen membrane | River water & wastewater       | 100  | 1    | [60]  |
| Potentiometry on ion-selective electrodes with PVC/thiacalix[4]arene membranes | River water                    | 120  | nr   | [61]  |
| Conductometric measurement of alkaline phosphatase activity in enzyme membranes on gold interdigitated electrodes | Tris-nitrate buffer            | 500  | 4    | [62]  |

*LoD: Limit of Detection; RSD: Relative Standard Deviation; nr: not reported; DPASV: Differential Pulse Anodic Stripping Voltammetry; SWASV: Square-Wave Anodic Stripping Voltammetry; LSASV: linear-scan anodic stripping voltammetry.

Around 50% of electrochemical sensor display a detection limit for cadmium below 1 μg/L [34-41] on modified carbon electrodes. Other micro-sensors give detection limits ranging from 1 μg/L [42-46] to 100–120 μg/L [60] and 500 μg/L [62] on enzymatic biosensors, 3.6 μg/L using anodic stripping
voltammetry on screen printed electrodes doped with bismuth nanoparticles [54] and 20 μg/L by differential pulse voltammetry through polyvinylchloride-2-nitrophenylethyl ether gel [58].

Table 3. Analytical characteristics of optical sensors for cadmium determination in water, published between 2007 and 2009.

| Method                                                                 | Tested sample            | LoD (mg/L) | RSD (%) | Ref. |
|------------------------------------------------------------------------|--------------------------|------------|---------|------|
| Absorbance of 4-hydroxy salophen on triacetyl cellulose membrane at 431 nm | Wastewater & river water | 0.06       | 2.9     | [63] |
| Fluorescence enhancement of porphyrin-terpyridine complex              | River waters             | 0.13       | 4.1     | [64] |
| Nine cross-reactive sensing fluorescent elements on micro-plate & data processed by pattern recognition | Mineral waters           | 0.56       | nr      | [65] |
| Photoluminescence enhancement of CdS:Mn/ ZnS Qdots in 1,10-diaza-18-crown-6 shell | Standard                 | 11         | nr      | [66] |
| Fluorescence enhancement of 8-hydroxyquinoline (319/410 nm)            | Standard                 | 3,000      | nr      | [67] |

*LoD: Limit of Detection; RSD: Relative Standard Deviation; nr: not reported; DPASV: Differential Pulse Anodic Stripping Voltammetry; SWASV: Square-Wave Anodic Stripping Voltammetry; LSASV: linear-scan anodic stripping voltammetry.

Optical sensors are two or three magnitude order less sensitive than electrochemical sensors. The most sensitive optical sensor displays a detection limit equal to 60 μg/L [63], then are following: 130 μg/L for fluorescent sensor [64] and 560 μg/L for the virtual sensor [65].

Even the detection limits of electrochemical sensors are still too high for water monitoring. The EQS values recommended by the WFD in freshwater range from 0.08 μg/L to 0.25 μg/L according to water hardness; INERIS publishes for cadmium, a PNEC equal to 0.21 μg/L [68] and the SEQ-Eau target value for an optimal water quality goes from 1 ng/L to 9 ng/L, according to water hardness [32]. Finally none of these micro-sensors was validated in a natural environment.

3.1.1. Mercury

Contrary to cadmium determination, for which electrochemistry is widely used, researchers seem to have preferred optical methods for mercury determination in water. Fifty-five articles deal with micro-sensors measuring mercury in water:

- Forty-three articles suggest measuring mercury by an optical means: molecular absorption (Table 4); and fluorescence (Table 5) or by chemiluminescence (two sensors). Among the optical methods, let us note the indirect method of Dittman et al. [69] based on the correlation between 254 nm absorbance of hydrophobic acid fraction of dissolved organic matter and mercury concentration. This method was successfully applied to waters of three different forested watersheds in New Hampshire, Vermont, and the State of New York (USA). It gives determination coefficients equal to, respectively, 0.96, 0.99 and 0.98 and its detection limit would be around 0.5 ng/L, corresponding to 0.05 absorbance unit. The authors attribute this correlation to the high content of reduced sulphur sites in hydrophobic acid fraction of organic matter;
Fifteen articles propose an electrochemical method (Table 6).

Among the mixed optical methods, let us point out two techniques:

- Lee and Mirkin’s method, associating DNA arrays using DNA-modified gold nanoparticle probes and a conventional flatbed scanner to measure scattered light, after silver amplification, gives a detection limit of 2 μg/L [70];

- The virtual sensor of Wang et al. [65] combining together nine cross-reactive sensing fluorescent elements on micro-plate with pattern recognition software in order to discriminate and quantify Hg in water. The sensor arrays are excited with a broadband UV lamp and four filters are used for emission detection: 380–500 nm $\lambda_{\text{max}}$ = 435 nm; 480–600 nm $\lambda_{\text{max}}$ = 525 nm; 523 nm and 580 nm. The array capacity was tested at different ranges of pH and at different cation concentrations using linear discriminant analysis. Quantitative analysis can be achieved with 93% accuracy in the concentration $\geq$20 mg/L [65].

### Table 4. Analytical characteristics of colorimetric sensors for mercury determination in water, published between 2007 and 2009.

| $\lambda_{ab}$ (nm) | Chromophore                                                                 | Tested sample     | LoD (μg/L) | RSD (%) | Ref. |
|---------------------|------------------------------------------------------------------------------|-------------------|------------|---------|------|
| 650                 | 2-Mercapto-2-thiazoline and chromo-ionophore/PVC membrane                     | River waters      | 0.01       | 0.76    | [71] |
| 580                 | 4-Phenyl-2,6-bis(2,3,5,6-tetrahydrobenzo[b] [1,4,7]-trioxonin-9-yl)pyrylium perchlorate/PVC membrane, (turn-on) | Shaft & fountain waters | 0.02       | 0.04    | [72] |
| 663                 | 2-Mercaptopyrimidine in PVC membrane (turn-off)                              | River waters      | 0.08       | 0.42    | [73] |
| 405                 | 3,30,5,50-Tetramethylbenzidine on DNA probe (turn off)                       | Spiked creek waters | 0.2        | nr      | [74] |
| 520                 | 4(2-Pyridylazo)resorcinol                                                   | Spiked water      | 0.22       | 5       | [75] |
| 450                 | Tetraphenylporphinetetrasulfonic acid on mesoporous monolith                 | Buffer pH 9       | 1.2        | 0.4     | [76] |
| 557                 | Tetrapyridine on “dip-sticks (turn-off)                                     | Standards         | 5          | nr      | [77] |
| 400/530             | Spiropyran probe (turn on).                                                  | Spiked tap water  | 20         | nr      | [78] |
| 429                 | 4-Hydroxysalophen                                                            | Tap & river water | 26         | 1.8     | [79] |
| 665                 | Hexathiacyclooctadecane                                                      | Tap & river water | 40         | 2.4     | [80] |
| 642                 | Squaraine dye derivatives                                                    | Standards         | 100        | nr      | [81] |
| 560                 | 1-[2-Pyridylazo]-2-naphthol in triacetyl cellulose                           | River & waste waters | 160        | 3.1     | [82] |
| 254                 | Hydrophobic acid fraction in DOC used as proxy of dissolved Hg              | River & lake water | 300        |         | [69] |
Table 4. Cont.

| λ_{ex}/λ_{em} (nm) | Chromophore | Tested sample | LoD (μg/L) | RSD (%) | Ref. |
|---------------------|-------------|---------------|------------|----------|------|
| 520/300 | Naphthalimide derivative on gold nanoparticles | Standard | 500 | nr | [83] |
| 490 | Cyclotrimeratylene derivative | River water | 1,000 | 0.9 | [84] |
| 530 | Sensitised alumina cladding and PLS model | Standards | 1,000 | | [85] |
| 542 | Azo-coupled macrocyclic dye, on a silica nanotube | Standards | 20,000 | nr | [86] |

*LoD: Limit of Detection; RSD: Relative Standard Deviation; nr: not reported.

Table 5. Analytical characteristics of fluorimetric sensors for mercury determination in water, published between 2007 and 2009.

| λ_{ex}/λ_{em} (nm) | Chromophore | Tested sample | LoD (μg/L) | RSD (%) | Ref. |
|---------------------|-------------|---------------|------------|----------|------|
| 510/581 | Rhodamine on thioglycolic acid modified gold nanoparticles (−) | River water | 0.01 | 1.2 | [87] |
| 485/535 | Polarization on DNA functionalized gold nanoparticles (+) | Spiked river water | 0.2 | nr | [88] |
| 500/550 | Rhodamine derivatives (+) | Spiked waters | 1 | nr | [89] |
| 475/510 | carboxyfluorescein on 4-[(4-(dimethylamino)phenylazo)benzoic acid binding on DNA probes | Pond water | 1 | nr | [90] |
| 401/538 | Naphthalimide derivative of 2,6-bis(aminomethyl)pyridine | Tap waters | 1.4 | 2.3 | [91] |
| 520/600 | Polythymine oligonucleotide T33, citrate-capped gold nanoparticles | Pond water | 2 | 8 | [92] |
| 273/519–527 | T–T mismatch base pairs, (−) | Spiked river water | 4 | | [93] |
| 425/646–603 | Prophirin-quinoline (turn-off at 646 nm and turn on at 603 nm) | Spiked river waters | 4.4 | nr | [94] |
| 490/510 | Oligonucleotides, DNA intercalators, and conjugated polymers | Standards | 6.4 | nr | [95] |
| 228–280/330 | CdS-encapsulated DNA nanocomposite (−) | Wastewater | 8 | | [96] |
| 438/673 | Porphyrin/PVC membrane (−) | Spiked river water | 8 | 4 | [97] |
| 273/519–527 | T–T mismatch base pairs (+) | Buffer | 8.4 | | [98] |
| 480/525 | DNA-functionalized gold nanoparticles & OliGreen | Spiked pond water | 10 | | [99] |
| 499/624 | Seminaphthofluorescein chromophore. (+) | River waters | 10 | 4.5 | [100] |
| 365/488 | Coumarinylalkyne (−) | Buffer pH 7.4 | 20 | | [101] |
| 458/534 | 2-[(Aminoethylthio)propylthio]ethanamine on 7-nitrobenzo-2-oxa-1,3-diazoloyl moieties (+) | Acetonitrile/water | 20 | | [102] |
| 415/ratio | Naphthalimide-porphyrin hybrid (+) | River waters | 20 | 4.4 | [103] |
| 525/650 | | | | | |
| 633/ratio | Polymer thiourea-thiadiazole-pyridine (+) | Water/Tetrahydrofuran | 22.6 | nr | [104] |
| 501/403 | | | | | |
| 490/591–520 | CdSe quantum dots surface-modified with triethanolamine | Standards | 36 | nr | [105] |
| 352/500 | Quinolinocycloglycoside derivative (−) | Standards | 60 | nr | [106] |
Two sensors are based on luminescence, the first one is based on bioluminescence on recombinant *E. Coli* immobilised on optical fibres [109]; and the second one is based on chemoluminescence of an iminophenol trimers [110]. Their detection limits are respectively 2.6 μg/L and 10 μg/L.

If we put aside the detection limit of Dittman *et al.*’s method [69] which would demand a validation on waters different to waters from forested watersheds (nitrate interference), the detection limits of the majority of these micro-sensors are still too high for an environmental application, but not too far from the “0.05 μg/L target”. Certain optical micro-sensors reach the detection limit of 0.2 μg/L by spectrometry [71,72,74] or fluorimetry [87,88], and electrochemical micro-sensors come down to the limit detection of 0.1 μg/L [38,111].

### Table 6. Analytical characteristics of electrochemical sensors for mercury determination in water, published between 2007 and 2009.

| Method                              | Tested sample                        | LoD (μg/L) | RSD (%) | Ref.   |
|-------------------------------------|--------------------------------------|------------|---------|--------|
| DPASV on Boron-doped diamond like carbon electrode | Standard pH 1                         | 0.002      | 10      | [112]  |
| DPASV on screen-printed carbon paste microelectrode chip | Standard solutions                  | 0.03       | nr      | [113]  |
| Amperometric measure of ammonia from urease on rhodinized carbon electrode | Standards                            | 0.1        | nr      | [38]   |
| DPSV on labeled DNA gold nanoparticles | Tap & river waters                   | 0.1        | 4       | [111]  |
| Cyclic voltammetry on invertase-glucose oxidase modified Pt electrode (inhibition) | Spiked waters                        | 2          | nr      | [53]   |
| Field Effect Transistor on single walled carbon nanotube sensor | Standards                            | 2          | nr      | [114]  |
| Potentiometry on 2-amino-6-purinethiol or 5-amino-1,3,4-thiadiazole-2-thiol/PVC membrane | Natural waters                       | 8.8        | 3       | [115]  |
| SWASV on 2-aminothiazole modified carbon paste electrode | Tap & waste waters                   | 12         | 10      | [116]  |
| Potentiometry on substituted thiourae-functionalized nanoporous silica | Wastewater                           | 14         | 4.5     | [117]  |
| DPSV on labeled DNA with a ferrocene on a gold electrode surface | Buffers                             | 20         | nr      | [118]  |
| Potentiometry on bis(benzoyl acetone) diethylene triamine/PVC membrane | Natural & waste waters               | 20         | 0.5     | [119]  |
Table 6. Cont.

| Method                                                                 | Tested sample    | LoD (μg/L) | RSD (%) | Ref.   |
|------------------------------------------------------------------------|-----------------|------------|---------|--------|
| Potentiometry on salophen modified carbon paste electrode              | Natural waters  | 30         | 0.8     | [120]  |
| LASV on Nitrogen doped tetrahedral amorphous carbon thin films/silicone | Standard pH 1    | 200        | nr      | [121]  |
| ASV on chitosan modified carbon paste electrode                        | Spiked waters   | 130        | 5       | [122]  |
| Chrono-amperometry on glucose oxidase in poly-o-phenylenediamine film (inhibition) | Standard        | 500        | 6       | [123]  |

*LoD: Limit of Detection; RSD: Relative Standard Deviation; nr: not reported; DPASV: Differential Pulse Anodic Stripping Voltammetry; SWASV: Square-Wave Anodic Stripping Voltammetry; LSASV: linear-scan anodic stripping voltammetry.

Only two micro-sensors reach the “0.05 μg/L target”, the first one with a detection limit 0.002 μg/L at pH 1 on diamond like carbon electrode [112] and the second one with a detection limit 0.03 μg/L but on acetate buffer at pH 4.2 on screen printed paste carbon electrode [113]. These micro-sensors are ready for the targeted or recommended values for water pollution control: WFD fixes a target value at 0.05 μg/L, but they are still not enough sensitive for reaching the SEQ-Eau target value: 0.007 μg/L [32]. Testing of these sensors for in situ mercury determination still remains to be done. None of these micro-sensors was evaluated in the field; only Dittman et al.’s method [69] should be applicable in the field with a commercial UV probe, of which spectral deconvolution algorithms should be fitted, and with a specific calibration.

3.1.2. Nickel

Only six articles (Table 7), among which two come from the same team, deal with nickel detection. Among these six papers, four use electrochemical methods: cyclic voltammetry [113,124], or conductometry [42,62], and two teams use optical methods – fluorimetry [65] or colorimetry [125].

Table 7. Analytical characteristics of sensors for nickel determination in water published between 2007 and 2009.

| Method                                                                 | Tested sample     | LoD (μg/L) | RSD (%) | Ref.   |
|------------------------------------------------------------------------|-------------------|------------|---------|--------|
| SWASV on bismuth-film electrode after complexation with dimethylglyoxime | River water       | 0.1        | 2.3     | [124]  |
| DPASV on carbon screen-printed micro-electrode chip                    | Acetate buffer    | 0.5        | nr      | [113]  |
| Conductometric measurement of alkaline phosphatase activity of the microalgae *Chlorella vulgaris* on two gold interdigitated electrodes | Wastewater        | 1          | nr      | [42]   |
| Colorimetry (ratio 540 nm/396 nm) of glutathione-stabilized silver nanoparticles | Standard          | 600        | nr      | [125]  |
| Conductometric measurement of alkaline phosphatase activity in enzyme membrane on gold interdigitated electrodes | Tris-nitrate buffer | 5,000     | 4       | [62]   |
Electrochemical methods give lower detection limits than optical methods. Only the electrochemical micro-sensors, once validated in laboratory, should be useful for nickel monitoring within the WFD framework (AA-EQS: 20 μg/L). Only the bismuth-film electrode micro-sensor [124] covers completely the INERIS or SEQ-Eau requirements, their target values being, respectively, 0.5 μg/L and 0.25 μg/L.

### 3.1.3. Lead

Thirty-six articles describe micro-sensors measuring lead in waters, the majority of them propose electrochemical methods (Table 8), only five articles present optical methods. The majority of the published electrochemical methods are voltammetric methods, mainly on modified carbon electrodes (paste or glassy carbon, graphite) with detection limits below the SEQ-Eau target value: 0.21 μg/L [34,40,126,127,128]. Turek et al., develop a virtual sensor founded on fuzzy logic data analysis of combined potentiometric signals from Ag-, Cu- and Pb-selective chalcocgenide glass sensors (AgIAsSe, CuAgAsSe, PbI2Ag2SAs2S3). This method recognizes an unknown metal in solutions with 100% probability, for heavy metal concentrations higher than 210 μg/L [129].

### Table 8. Analytical characteristics of electrochemical sensors for lead determination in water, published between 2007 and 2009.

| Method                                      | Tested samples          | LoD (μg/L) | RSD (%) | Ref. |
|---------------------------------------------|-------------------------|------------|---------|------|
| DPASV on multiwalled carbon nanotubes/Bi film modified glassy carbon electrode | Tap & river water       | 0.1        | 4.1     | [34] |
| Potentiometry on 5,5-dithiobis(2-nitrobenzoic acid)/PVC membrane | Mine water              | 0.12       | 20      | [128]|
| SWASV on hydroxyapatite modified carbon paste electrode   | Tap & wastewater        | 0.16       | 4.1     | [126]|
| SWASV on antimony film carbon paste electrode   | Lake water              | 0.2        | 1.2     | [40]  |
| LASV on graphite felt electrode              | Standards               | 0.2        | 15      | [127]|
| DPASV on carbon paste electrode modified with biomolecular chitosan | Tap water               | 0.3        | 3.5     | [130]|
| SWASV on bismuth-film electrodes             | River water             | 0.5        | 4.4     | [43]  |
| DPASV on bismuth film/graphite electrode     | Acetate pH 4            | 0.5        | nr      | [36]  |
| DPASV on bismuth/poly(p-aminobenzene sulfonic acid) film electrode | Tap water               | 0.80       | 3.9     | [39]  |
| Method                                      | Supporting Electrode | Supporting Electrolyte | pH  | RSD  | Ref |
|---------------------------------------------|-----------------------|-------------------------|-----|------|-----|
| SWASV on carbon disk screen-printed electrode with Bi ions | Wastewater | 0.9 | 7.4 | [54] |
| Conductometric measurement of alkaline phosphatase activity of the microalgae *Chlorella vulgaris* on two gold interdigitated electrodes | Wastewater | 1 | nr | [42] |
| SWASV on polymer-modified glassy carbon electrode | Plating wastewater | 1 | 2.5 | [131] |
| DPASV on boron-doped diamond | Acetate buffer | 1.1 | nr | [35] |
| DPASV on glassy carbon electrode modified with *p*-tert-butyli-thiacalix[4]arene | Lake & tap waters | 1.7 | 2.9 | [49] |
| SWASV on screen-printed graphite electrode | Seawater | 1.8 | 4.9 | [52] |
| SWASV on bismuth nanoparticle modified boron doped diamond | Standard pH 1.2 | 1.9 | nr | [50] |
| SWASV on glassy-carbon electrodes modified with Nafion & thiol monolayer composite on mesoporous supports | River & ground waters | 2.7 | 5 | [51, 132] |
| LASV on a zeolite NH4-Y modified carbon paste electrode | Groundwater & industrial wastewater | 3.6 | 7 | [44] |
| SWASV on carbon paste electrode modified with 2-aminothiazole | Tap water | 4.5 | 10 | [116] |
| SWASV on nitrogen doped diamond-like carbon microelectrode array | Acetate buffer pH 4 | 4.6 | nr | [36] |
| Cyclic voltammetry of invertase–glucose oxidase activities on platinum microelectrode | Phosphate buffer | 6.2 | nr | [53] |
| ASV on screen-printed Bismuth oxide/graphite electrode | Wastewater | 8 | 5.6 | [57] |
| SWASV on bismuth electrode | Pore & groundwater | 8 | 15 | [56] |
| LSASV on antimony nanoparticle modified boron doped diamond | Standard pH 1 | 18.5 | nr | [59] |
| Potentiometry on polyaminoanthraquinone microparticle/PVC membrane | Spiked rain & tap waters | 160 | nr | [133] |
| LASV on Nitrogen doped tetrahedral amorphous carbon thin films/silicone | Standard pH 1 | 210 | nr | [121] |
| SWASV on polymer-modified glassy carbon electrode | Plating wastewater | 400 | 2.8 | [45] |
| Potentiometry on substituted macrocyclic diamides/PVC membrane | Standards | 410 | | [134] |
| Conductometric measurement of alkaline phosphatase activity in enzyme membrane on gold interdigitated electrodes | Standards | 40,000 | 4 | [62] |

*LoD: Limit of Detection; RSD: Relative Standard Deviation; nr: not reported; DPASV: Differential Pulse Anodic Stripping Voltammetry; SWASV: Square-Wave Anodic Stripping Voltammetry; LSASV: linear-scan anodic stripping voltammetry.
Table 9. Analytical characteristics of optical sensors for lead determination in water published between 2007 and 2009.

| Method                                                                 | Tested sample               | LoD (μg/L) | RSD (%) | Ref. |
|------------------------------------------------------------------------|-----------------------------|------------|---------|------|
| Fluorimetry (475/518nm) on thrombin-binding aptamer probe labeled with carboxyfluorescein & 4-([4-(dimethylamino)phenyl]azo)benzoic acid (turn on) | Pond water                  | 0.1        | 1.3    | [90] |
| Fluorimetric scanning of metal dependent DNazymes microarray           | Spiked river water          | 2          | 6.7    | [135]|
| Colorimetry (434 nm) of 4-hydroxysalophen on cellulose membrane         | River & wastewater          | 18         | 2.1    | [136]|
| Fluorimetry (365/418 nm) on polyfluorene with two benzo-18-crown-6 side chains (turn off) | Standards                  | 1,000      | nr     | [137]|
| Colorimetry (530 nm) on diphenylcarbazone/PVC membrane                | Natural & wastewater        | 1,300      | nr     | [138]|

*LoD: Limit of Detection; RSD: Relative Standard Deviation; nr: not reported; DPASV: Differential Pulse Anodic Stripping Voltammetry; SWASV: Square-Wave Anodic Stripping Voltammetry; LSASV: linear-scan anodic stripping voltammetry.

Predicted Non Effect Concentration (PNEC) for lead, advocated by INERIS (PNEC: 5 μg/L), is only achieved using voltammetric sensors ([35,39,43,44,49,51,52,54,130-132] and one conductometric biosensor based on *Chlorella vulgaris* [42]. However, this sensor shows a poor specificity. Indeed, heavy-metal ions acting as algal alkaline phosphatase inhibitors, so cadmium, cobalt, nickel and lead exhibit the same detection limit (1 μg/L).

Finally among published optical methods (Table 9), the most sensitive micro-sensor uses DNA probes and fluorescence quenching or turn-off. Pb(II) is measured by ADNzyme activation and DNA cleavage of two fluorescent cyanine probes: Cy3 (550/570 nm) for the detection and Cy5 (650/670 nm) for the reference [135]. Liu *et al.* [90] use a thrombin-binding aptamer probe labelled with donor carboxyfluorescein and quencher 4-([4-(dimethylamino)phenyl]azo)benzoic acid at its 5’ and 3’ termini, respectively. These two optical methods give acceptable detection limits for water monitoring, with respectively: 2 μg/L [135] and 0.1 μg/L [90]. Two other optical methods are colorimetric ones and present too high detection limits: 18 μg/L [136] and 1.3 mg/L [138].

All the aforementioned sensors are adapted to lead monitoring in water according to the WFD criterion: target value at 7 μg/L. However none of these micro-sensors is still at the evaluation stage and ruggedness and hardiness will have to guide selection of the micro-sensors fit for field validation.

3.1.4. Conclusions on metal determination

Mainly because of environmental regulations, the current research on sensors for metal determinations is under a kind of double bind: mercury elimination from devices and keeping the detection limits of mercury electrodes. This particularly stimulating situation will lead to new greener micro-sensors. These new generations of sensors are still in their infancy and many approaches are being explored. The electrochemical approach is the privileged technique by the four fifths of the
authors, at least for Cd, Ni and Pb. For the mercury titration there is an inverse proportion with dominance in 80% of the optical approach. It is worthy noting that representing about 60% of published papers, the research efforts in the WFD metal determination seem at present to be to concentrate on mercury detection. The activity seems more particularly active in the research for new chromophores more specific and more sensitive, and of original couplings between chromophore and ionophore. Finally, some articles investigate the potential of virtual sensors, otherwise known as “soft sensors” or “smart sensors”, in heavy metal monitoring. These sensors consist of an array of simple and reliable sensors that are not analyte-specific but can be linked by a computer programmed to process certain sample features and build a proxy of the “unsensed” metal [65,129]. Multivariate calibration, a statistically inspired modification of partial least square method, is applied to DPASV voltammograms acquired on carbon screen-printed electrodes. This data processing leads to better overall root mean square error of prediction values for Cd and Pb. The authors propose to investigate the application of artificial neural networks to the voltammograms in order to reduce the errors and to improve the number of target metals [139]. Until now, their detection limits are too high, and research should be carried out in order to make them operational tools in the field.

4. Organic Substances

Among priority substances listed in Appendix II of the Common Decision taken on 20 December, 2007 by the Council of Europe [2], 36 are organic substances, the five remaining being metals (Cd, Ni, Pb and Hg) and an organotin. Organic substances can be grouped in main chemical or usage groups: 17 pesticides, 10 chlorinated solvents, eight PAH and miscellaneous organic substances as alkylphenols, detergents, brominated diphenyl ether, aryl-halides and benzene. Table 10 summarises the superior limit concentrations recommended or statutory in freshwater.

Table 10. Summary of the superior limit concentrations (μg/L) in organic substances, recommended or statutory in freshwater.

|                | Superficial Water | Drinking Water |
|----------------|-------------------|----------------|
|                | WFD [2] AA-EQS    | SEQ-Eaux [32]  | Order in Council 2001-1220 [33] | SEQ Underground water |
| Benzene        | 10                | 0.5            | 1.0                        | 0.5                   |
| Chloroform     | 2.5               | 1.2            | 100                        | 5                     |
| Atrazine       | 0.6               | 0.02           | 0.1                        | 0.05                  |
| Isoproturon    | 0.3               | 0.02           | 0.1                        | 0.05                  |
| Chlorthrinphos | 0.1               | 0.0003         | 0.1                        | 0.05                  |
| Chlorpyrifos   | 0.03              | 0.00005        | 0.1                        | 0.05                  |
| DDTPp’         | 0.01              | 0.0002         | 0.1                        | 0.05                  |

*AA-EQS: Environmental quality standards expressed as an annual average value. SEQ-Eau : Système d'Evaluation de la Qualité de l'eau (Water Quality Evaluation System) developed by French Water Agencies.
However the scientific publications concerning priority WFD organic substance determinations by means of micro-sensors represent a more modest proportion, than that dedicated to four WFD metals. During years 2007–2009 we counted only two dozens of papers, mainly on detection of organophosphates and of some carbamates (Table 11). Among these, twelve articles present electrochemical methods on modified electrodes, among which seven enzymatic biosensors based on choline esterase activity. Other micro-sensors are intended to measure atrazine [140-142], isoproturon [143], paraquat [144] or DDT-like compounds [145]. Three articles propose sensors for solvent determination in water: two based on infrared spectroscopy and one on impedance spectrometry.

4.1. Organophosphates and Carbamates

Among organophosphate pesticides (Table 11) only chlorpyrifos appears among the thirty-three WFD substances, with an AA-EQS of 0.03 μg/L. However the proposed colorimetric method on gold nanoparticles presents high detection limits of several orders of magnitude for the titration of chlorpyrifos and malathion (20 μg/L and 100 μg/L, respectively). [146]. Acetylcholine esterase activity monitoring methods using voltammetry developed by Zhao et al., [147] and by Yin et al., [148] allow to reach lower concentrations, respectively: 0.5 ng/L for paraoxon and 1 ng/L for parathion [147], 6 ng/L for paraoxon methyl and 7 ng/L for carbofuran [148]. These methods would deserve to be tested on both WFD organophosphates: chlorpyrifos and chlorfenvinphos. Nevertheless these biosensors determine the total concentration of organophosphates and carbamate pesticides, and not a specific compound. Now, the definition of good chemical status in the WFD imposes the measurement of priority organic substance concentrations and not the measurement of toxic effects.

### Table 11: Micro-sensors for organophosphate and carbamates (in italics) determination in water. WFD priority organic substance in bold type.

| Method | Compound | LoD | Ref. |
|--------|----------|-----|------|
| Colorimetry on gold nanoparticles | Chlorpyrifos, Malathion | 20 μg/L, 100 μg/L | [146] |
| Guided shear horizontal surface acoustic wave devices on LiTaO₃ | Phosmet, Parathion | 5 mg/L, 2 mg/L | [149] |
| Voltammetry on clay modified electrodes containing Ni₂Al-NO₃ | Glyphosate, Glufosinate | 169 μg/L, 905 μg/L | [150] |
| Amperometric activity measurement of acetylcholinesterase immobilized on screen-printed graphite electrode | Chlorpyrifos | 2 μg/L | [151,152] |
| Voltammetry on glassy carbon electrode modified with a poly-L-cysteine film | Methyl parathion | 1.7 μg/L | [153] |
| Amperometric activity measurement of acetylcholinesterase immobilized on gold nanoparticles and silk fibroin modified platinum electrode | Methyl paraoxon, Carbofuran, Phoxim | 6 ng/L, 7 ng/L, 0.6 μg/L | [148] |
| Amperometric activity measurement of acetylcholinesterase immobilized on calcium carbonate-chitosan composite film | Methyl parathion | 1 μg/L | [154] |
Table 11. Cont.

| Amperometric activity measurement of acetylcholinesterase and choline oxidase within separate hybrid mesoporous silica membranes | Diazinon-oxon | 0.37 μg/L | [155] |
| Amperometric activity measurement of acetylcholinesterase on gold-platinum bimetallic nanoparticles onto 3-amino-propyltriethoxy silane modified glassy carbon electrode | Paraoxon ethyl Sarin Aldicarb | 9.5 μg/L 6 μg/L 48 μg/L | [156] |
| Amperometric activity measurement of acetylcholinesterase on poly(dimethosiloxane)-poly(diallydimethylammonium)/gold nanoparticles composite film | Paraoxon Parathion | 0.5 ng/L 1.0 ng/L | [147] |
| Voltammetry on nano-alumine film modified electrode | Parathion | 0.3 μg/L | [157] |
| Amperometric reactivation measurement of cholinesterase from organophosphorus-inhibited rat saliva on carbon nanotube modified screen printed carbon electrode | Paraoxon | 0.14 μg/L | [158] |

*LoD: Limit of Detection.

4.2. Other pesticides

Among other methods proposed for pesticide determination (Table 12), three methods are proposed for triazine measurement. Pardieu et al. [140] presented an electrochemical micro-sensor, based on a molecularly imprinted conducting polymer, deposited on a platinum electrode, able to detect, by cyclic voltammetry, triazines (atrazine, terbutylazine and simazine) and to measure atrazine with a detection limit of 4.5 μg/L. An immunoassay based on a commercially available surface plasmon resonance (SPR) biosensor was proposed. Measurement can be performed in 25 minutes, including the regeneration cycle, and its detection limit in laboratory is 20 ng/L and 26 ng/L in a river sample [141]. A microbioreactor and integrated sensors for the online measurement of oxygen production was used to measure benzalkonium chloride and atrazine effects on the macrophyte Elodea canadensis. No observable adverse effect concentration (NOAEC) for atrazine is 10 μg/L [142]. Gouzy et al. [143] developed an immunosensor based on SPR for the measurement of isoproturon. The rat monoclonal anti-isoproturon antibody was reversibly immobilized through the use of a capture mouse anti-rat monoclonal antibody, which was covalently immobilized on the sensor chip surface. The detection limit could have reach 0.1 μg/L, but the operational range goes from 1.3 μg/L to 16.3 μg/L (inhibition from 20 to 80%). Lee et al [144] measured morphology and resonance characteristics of human hepatoma cell line cultured onto an indium tin oxide layer on the surface of a quartz crystal modified with a collagen film, for the study of the effect of paraquat (2.7 μg/μL) through resonance frequency and resonance resistance responses. The system gives a qualitative response and allows the visualization of the action of paraquat on cells. Finally, an immunosensor based on commercially available SPR has been developed for the monitoring of DDT, its metabolites and analogues in real water samples. Low detection limits are attained for DDT-selective: 15 ng/L; and DDT group-selective immunoassays: 31 ng/L [145].
Table 12. Micro-sensors for pesticide determination in water, other than organophosphate and carbamates. WFD priority organic substances in bold type.

| Method                                                                 | Compound   | LoD       | Ref. |
|------------------------------------------------------------------------|------------|-----------|------|
| Voltammetry on conducting MIP deposited on an platinum electrode       | Atrazine   | 4.5 μg/L  | [140]|
| Surface plasmon resonance (SPR) on monoclonal anti-bodies immobilized on a gold sensor surface | Atrazine   | 20 ng/L   | [141]|
| Oxygen production and fluorescence measures on the algae *Elodea canadensis* culture | Atrazine   | 10 μg/L   | [142]|
| Surface plasmon resonance (SPR) on monoclonal anti-bodies immobilized on sensor chip surface | Isoproturon | 0.1 μg/L | [143]|
| Resonance characteristics hepatoma cultured on an indium tin oxide surface of quartz crystal | Paraquat   | 2.7 mg/L  | [144]|
| Surface plasmon resonance (SPR) on monoclonal antibodies on gold-thin layer | DDT        | 15 ng/L   | [145]|

*LoD: Limit of Detection.

4.3. Solvents

The restricted number of solvent sensors developed (Table 13) present detection limits higher than the WFD and SEQ-Eau’s target values (Table 10), respectively 10 μg/L and 0.5 μg/L for benzene and 2.5 μg/L and 1.2 μg/L for chloroform.

Table 13. Micro-sensors for solvent determination in water.

| Method                                                                 | Compound   | LoD       | Ref. |
|------------------------------------------------------------------------|------------|-----------|------|
| Infrared spectroscopy on polydimethylsiloxane (PDMS) membrane         | Benzene    | 0.6 mg/L  | [159]|
| Mid-infrared spectroscopy on 2-(2-hydroxy-5-tert-octylphenyl)benzotriazol/PVC membrane | Benzene    | 5.0 mg/L  | [160]|
| Impedance spectrometry on sensor array made up with electrodeposited polythiophene films onto interdigitated gold electrodes | Chloroform | 0.1 mg/L  | [161]|

*LoD: Limit of Detection

Finally, Kurup [162] describes a virtual sensor constituted of an array of seven SnO₂ micro-sensors doped with different impurities (as palladium or platinum) and equipped with a gas sampling membrane and integrated into a probe used for the volatile organic pollutant detection in underground environment. This technology supplies at the moment qualitative results (three levels: low, average and high), which must be then confirmed by conventional analyses in laboratory.

5. Conclusions

As noticed above, 81% of the publications appeared in 2007–2009 concern only 12% of the priority substances included in the WFD list, namely metals (e.g., Cd, Hg, Ni, Pb). The origin of this disparity
already noticed in the production is doubtlessly attributable to the heterogeneousness of chemical structures listed in WFD list which exceeds the financial capacity for sensor development or imposes one weakly profitable development of specific micro-sensor for each priority substance. The fact that only the organophosphates and carbamates are subject of a relatively important number of publications among those dedicated to organic substances (57%), tends to confirm this origin. Indeed these sensors are based on acetylcholinesterase inhibition by organophosphate and carbamates. So, the conception of micro-sensors measuring biological effects rather than concentrations could constitute an innovative way allowing the release from constraint of the development of substance specific micro-sensors. However the notion of “Environmental Quality Standards” in the WFD sense imposes the measurement of specific concentrations and not some effects. This normative aspect of the Directive establishes a strong constraint in the research for new analytical devices.

None of articles published during 2007–2009 presents a micro-sensor totally validated in the laboratory and ready for tests under real field conditions. Research is mainly focused on the sensitive part of the micro-sensors: the receptor. Now, even if progress still remains to achieve, in particular to lower the limit of detection, the principles of detection do not seem to constitute the main limiting factor the development of environmental micro-sensors. The sensitivities of the best cadmium or mercury sensors exhibit detection limits respectively five and two folds higher than SQE target values. It is too high for in situ measurement in natural waters, but these sensors could be right now used for the industrial wastewater control (e.g., electroplating plants). During the wait for a better sensitivity, these mercury-free sensors could be associated to concentration devices in lab-on-a-chips, in order to lower the detection limits.

On the other hand, receptor ruggedness to environmental conditions must be improved, in particular concerning their fouling resistance; technologies such as surface passivation, or ultrasound cleaning of the sensitive surface, should allow progress in this domain. This point constitutes the first technological obstacle to be overcome, before going into long-term tests in real environments.

Other scientific and technological obstacles to overcome in order to build operational micro-sensor networks are at the transducer and the transmitter levels. Setup up a micro-sensor in the natural environment requires an infrastructure capable of fuelling it with energy, watching it and collecting data. This means that skills outside the fields of chemistry, such as physics, electronics and computing, which will be required in order to build a complete in situ measurement chain. The main axes of progress must be centred on the following points:

- Miniaturization: pursue the integration of the various modules (receptor, transducer and transmitter) on the same chip. It leads to a decrease of the energy consumption and seems to have, at least on the conductometric electrodes, a beneficial effect on the sensitivity. This miniaturization requires for skills in micro-technology;
- Communication: assure the communication between the micro-sensors and the readout station and between the micro-sensors. The network should have the possibility of positioning these sensors (search for micro-sensors scattered after a flood in particular), of verifying the state of its communications with the readout station and its neighbour micro-sensors, of validating the quality of its data before their transmission, of alerting in
case of abnormal situation. Two wireless communication modes should be studying: ultrasound-based or radio frequencies;

- Autonomy: decrease the energy consumption or develop possibilities of in situ energy supply. Sedimentary microbial fuel cells or marine turbines would be technologies that should be investigated;

- Eco-design: integrate the possible impact of the chosen technology on the environment, as well as life cycle of the micro-sensor, and principles of measurement. Indeed in the eventuality of a loss of the material in the environment, the micro-sensor composition has to banish the use of well-known toxic or dangerous matter for the environment. This point concerns all devices introduced into the environment: we have to minimize as much as possible any toxic impact of our devices. Indeed, the WFD [1] demands, for priority hazardous substances from human activities (as cadmium or mercury), the cessation or phasing out of discharges, emissions and losses into water before 2020. This regulation coming into force in the Member States, the use of mercury is banished in the short-term. Also, development of new devices using priority hazardous substances leads to a commercial dead-end, and a waste of time and money: it cannot be used in Europe. Here and now, the regulatory requirements must be included in the design of new monitoring devices and we have to minimise the potential toxic impact of all components used to build efficient monitoring sensor network platform. Clearly, there is plenty of room for progression.

Finally it is advisable to mention the necessity of developing data processing technologies to manage in an optimal way the considerable data flows produced by a micro-sensor network. There are very significant challenges for the micro-sensor research community for delivering sensing platforms that are appropriate for integration into scaled-up deployments in terms of sustainability, cost, and reliability. Calls for proposals should centre on the conception of complete micro-sensor networks (material and software) and on the emergence of projects having as a global objective an operational monitoring network, from the receptors to the management computer.

Acknowledgments

Authors thank ONEMA (The French National Agency for Water and Aquatic Environment) for its financial support.

References

1. JOL Directive 2000/60/CE. du Parlement européen et du Conseil du 23 octobre 2000 établissant un cadre pour une politique communautaire dans le domaine de l’eau. Directive 2000/60/CE, du Parlement européen et du Conseil : Luxembourg, Germany, 2000.

2. JOL Directive 2008/32/CE. du Parlement européen et du Conseil du 11 mars 2008 modifiant la directive 2000/60/CE établissant un cadre pour une politique communautaire dans le domaine de l’eau; en ce qui concerne les compétences d’exécution conférées à la Commission. Directive 2008/32/CE, du Parlement européen et du Conseil : Luxembourg, Germany, 2008; pp. 60-61.
3. Braungardt, C.B.; Achterberg, E.P.; Axelsson, B.; Buffle, J.; Graziottin, F.; Howell, K.A.; Illuminati, S.; Scarponi, G.; Tappin, A.D.; Tercier-Waeber, M.L.; Turner, D. Analysis of dissolved metal fractions in coastal waters: An inter-comparison of five voltammetric in situ profiling (VIP) systems. *Mar. Chem.* 2009, 114, 47-55.

4. Greenwood, R.; Mills, G.A.; Roig, B. Introduction to emerging tools and their use in water monitoring. *TrAC Trends Anal. Chem.* 2007, 26, 263-267.

5. JOL Décision n° 2455/2001/CE du Parlement européen et du Conseil du 20 novembre 2001 établissant la liste des substances prioritaires dans le domaine de l'eau et modifiant la directive 2000/60/CE. Décision n° 2455/2001/EC, du Parlement européen et du Conseil : Luxembourg, Germany, 2001; pp. 1-5.

6. JOC Position Commune (CE) n° 3/2008 du 20 décembre 2007 arrêtée par le Conseil, statuant conformément à la procédure visée à l'article 251 du traité instituant la Communauté européenne, en vue de l'adoption d'une directive du Parlement européen et du Conseil établissant des normes de qualité environnementale dans le domaine de l'eau et modifiant les directives 82/176/CEE, 83/513/CEE, 84/156/CEE, 84/491/CEE, 86/280/CEE et 2000/60/CE. *Position Commune n° 3/2008*, du Parlement européen et du Conseil : Luxembourg, Germany, 2008; pp. 1-15.

7. Johnson, K.S.; Needoba, J.A.; Riser, S.C.; Showers, W.J. Chemical sensor networks for the aquatic environment. *Chem. Rev.* 2007, 107, 623-640.

8. Pejcic, B.; Eadington, P.; Ross, A. Environmental monitoring of hydrocarbons: A chemical sensor perspective. *Environ. Sci. Technol.* 2007, 41, 6333-6342.

9. Bosch, M.E.; Sanchez, A.J.R.; Rojas, F.S.; Ojeda, C.B. Recent development in optical fiber biosensors. *Sensors* 2007, 7, 797-859.

10. Lieberzeit, P.A.; Dickert, F.L. Sensor technology and its application in environmental analysis. *Anal. Bioanal. Chem.* 2007, 387, 237-247.

11. Reimers, C.E. Applications of microelectrodes to problems in chemical oceanography. *Chem. Rev.* 2007, 107, 590-600.

12. Tercier-Waeber, M.L.; Taillefert, M. Remote in situ voltammetric techniques to characterize the biogeochemical cycling of trace metals in aquatic systems. *J. Environ. Monitor.* 2008, 10, 30-54.

13. Tercier-Waeber, M.L.; Confalonieri, F.; Koudelka-Hep, M.; Dessureault-Rompre, J.; Graziottin, F.; Buffle, J. Gel-integrated voltammetric microsensors and submersible probes as reliable tools for environmental trace metal analysis and speciation. *Electroanal.* 2008, 20, 240-258.

14. Lange, K.; Rapp, B.E.; Rapp, M. Surface acoustic wave biosensors: A review. *Anal. Bioanal. Chem.* 2008, 391, 1509-1519.

15. Moreno-Garrio, I. Microalgae immobilization: Current techniques and uses. *Bioresource Technol.* 2008, 99, 3949-3964.

16. Jones, S.E.W.; Compton, R.G. Stripping analysis using boron-doped diamond electrodes. *Curr. Anal. Chem.* 2008, 4, 170-176.

17. Jaffrezi-Prenault, N.; Dzyadevych, S.V. Conductometric microbiosensors for environmental monitoring. *Sensors* 2008, 8, 2569-2588.
18. Seidel, M.; Niessner, R. Automated analytical microarrays: A critical review. *Anal. Bioanal. Chem.* **2008**, *391*, 1521-1544.

19. Palchetti, I.; Mascini, M. Nucleic acid biosensors for environmental pollution monitoring. *Analyst* **2008**, *133*, 846-854.

20. Johnson-White, B.; Harmon, H.J. Optical Enzyme-Based Sensors for Reagentless Detection of Chemical Analytes, In *Antiterrorism & Homeland Defense: Polymers & Materials*; Reynolds, J.G.; Lawson, G.E.; Koester, C.J., Eds.; American Chemical Society: Washington, DC, USA; 2007, pp. 57-70.

21. Nolan, E.M.; Lippard, S.J. Tools and tactics for the optical detection of mercuric ion. *Chem. Rev.* **2008**, *108*, 3443-3480.

22. Diamond, D.; Coyle, S.; Scarmagnani, S.; Hayes, J. Wireless sensor networks and chemo-/biosensing. *Chem. Rev.* **2008**, *108*, 652-679.

23. Strobl, R.O.; Robillard, P.D. Network design for water quality monitoring of surface freshwaters: A review. *J. Environ. Manage.* **2008**, *87*, 639-648.

24. Bogue, R. Environmental sensing: Strategies, technologies and applications. *Sensor Rev.* **2008**, *28*, 275-282.

25. Jaffrezic-Renault, N. Analytical electrochemistry for environment: electrochemical microsensors for the in situ monitoring of pollutants. *Actual. Chimique.* **2009**, *52*, 52-55.

26. Baruah, S.; Dutta, J. Nanotechnology applications in pollution sensing and degradation in agriculture: A review. *Environ. Chem. Lett.* **2009**, *7*, 191-204.

27. Pesavento, M.; Alberti, G.; Biesuz, R. Analytical methods for determination of free metal ion concentration, labile species fraction and metal complexation capacity of environmental waters: A review. *Anal. Chim. Acta* **2009**, *631*, 129-141.

28. Reardon, K.F.; Zhong, Z.; Lear, K.L. Environmental Applications of Photoluminescence-Based Biosensors. In *Optical Sensor Systems in Biotechnology*; Springer-Verlag: Berlin, Germany, 2009; Volume 116, pp. 99-123.

29. Leray, I.; Valeur, B. Calixarene-based fluorescent molecular sensors for toxic metals. *Eur. J. Inorg. Chem.* **2009**, *3525-3535.

30. Selid, P.D.; Xu, H.Y.; Collins, E.M.; Face-Collins, M.S.; Zhao, J.X. Sensing mercury for biomedical and environmental monitoring. *Sensors* **2009**, *9*, 5446-5459.

31. David, A.; Fenet, H.; Gomez, E. Alkylphenols in marine environments: Distribution monitoring strategies and detection considerations. *Mar. Pollut. Bull.* **2009**, *58*, 953-960.

32. RMC SEQ-Eau. système d'évaluation de la qualité de l'eau des cours d'eau (Version 2); 21 march 2003, 2003; p 40.

33. JO Décret n°2001-1220 du 20 décembre 2001 relatif aux eaux destinées à la consommation humaine, à l'exclusion des eaux minérales naturelles. Décret n°2001-1220 22 December 2001, 20381-20399.

34. Deng, W.F.; Tan, Y.M.; Fang, Z.F.; Xie, Q.J.; Li, Y.Y.; Liang, X.L.; Yao, S.Z. ABTS-Multiwalled carbon nanotubes nanocomposite/Bi film electrode for sensitive determination of Cd and Pb by differential pulse stripping voltammetry. *Electroanal.* **2009**, *21*, 2477-2485.

35. El Tall, O.; Jaffrezic-Renault, N.; Sigaud, M.; Vittori, O. Anodic stripping voltammetry of heavy metals at nanocrystalline boron-doped diamond electrode. *Electroanal.* **2007**, *19*, 1152-1159.
36. Rehacek, V.; Hotovy, I.; Vojs, M.; Mika, F. Bismuth film electrodes for heavy metals determination. *Microsyst. Technol.* **2008**, *14*, 491-498.

37. El Mhammedi, M.A.; Achak, M.; Najih, R.; Bakasse, M.; Chtaini, A. Micro-extraction and trace determination of cadmium by square wave voltammetry at the carbon paste electrode impregnated with Ca$_{10}$(PO$_4$)$_6$(OH)$_2$. *Mater. Chem. Phys.* **2009**, *115*, 567-571.

38. Pal, P.; Bhattacharyay, D.; Mukhopadhyay, A.; Sarkar, P. The detection of mercury, cadmium, and arsenic by the deactivation of urease on rhodinized carbon. *Environ. Eng. Sci.* **2009**, *26*, 25-32.

39. Wu, Y.; Li, N.B.; Luo, H.Q. Simultaneous measurement of Pb, Cd and Zn using differential pulse anodic stripping voltammetry at a bismuth/poly(p-aminobenzene sulfonic acid) film electrode. *Sensor. Actuat. B-Chem.* **2008**, *133*, 677-681.

40. Tesarova, E.; Baldrianova, L.; Hocevar, S.B.; Svancara, I.; Vytras, K.; Ogorevc, B. Anodic stripping voltammetric measurement of trace heavy metals at antimony film carbon paste electrode. *Electrochim. Acta* **2009**, *54*, 1506-1510.

41. Tian, Y.Q.; Li, N.B.; Luo, H.Q. Simultaneous determination of trace zinc (ii) and cadmium (ii) by differential pulse anodic stripping voltammetry using a MWCNTs-NaDBS modified stannum film electrode. *Electroanal.* **2009**, *21*, 2584-2589.

42. Berezhetskyy, A.L.; Durrieu, C.; Nguyen-Ngoc, H.; Chovelon, J.M.; Dzyadevich, S.; Tran-Minh, C. Conductometric biosensor based on whole-cell microalgae for assessment of heavy metal in wastewater. *Biopolym. Cell* **2007**, *23*, 511-518.

43. Kokkinos, C.; Economou, A.; Raptis, I.; Efstatithiou, C.E. Lithographically fabricated disposable bismuth-film electrodes for the trace determination of Pb(II) and Cd(II) by anodic stripping voltammetry. *Electrochim. Acta* **2008**, *53*, 5294-5299.

44. Senthilkumar, S.; Saraswathi, R. Electrochemical sensing of cadmium and lead ions at zeolite-modified electrodes: Optimization and field measurements. *Sensor. Actuat. B-Chem.* **2009**, *141*, 65-75.

45. Vedhi, C.; Selvanathan, G.; Arumugam, P.; Manisankar, P. Electrochemical sensors of heavy metals using novel polymer-modified glassy carbon electrodes. *Ionics* **2009**, *15*, 377-383.

46. Guedri, H.; Durrieu, C. A Nafion/BSA based conductometric algal whole cell biosensor for heavy metal monitoring. *Environ. Sci. Technol.* **2009**, *42*, 623-628.

47. Guedri, H.; Durrieu, C. A self-assembled monolayers based conductometric algal whole cell biosensor for water monitoring. *Microchim. Acta* **2008**, *163*, 179-184.

48. Cugnet, C.; Zaouak, O.; Rene, A.; Pecheyran, C.; Potin-Gautier, M.; Authier, L. A novel microelectrode array combining screen-printing and femtosecond laser ablation technologies: Development, characterization and application to cadmium detection. *Sensor. Actuat. B-Chem.* **2009**, *143*, 158-163.

49. Zheng, H.; Yan, Z.; Dong, H.; Ye, B. Simultaneous determination of lead and cadmium at a glassy carbon electrode modified with Langmuir-Blodgett film of p-tert-butylthiacalix[4]arene. *Sensor. Actuat. B-Chem.* **2007**, *120*, 603-609.

50. Toghill, K.E.; Wildgoose, G.G.; Moshar, A.; Mulcahy, C.; Compton, R.G. The fabrication and characterization of a bismuth nanoparticle modified boron doped diamond electrode and its application to the simultaneous determination of cadmium(II) and lead(II). *Electroanal.* **2008**, *20*, 1731-1737.
51. Yantasee, W.; Charnhattakorn, B.; Fryxell, G.E.; Lin, Y.; Timchalk, C.; Addleman, R.S. Detection of Cd, Pb, and Cu in non-pretreated natural waters and urine with thiol functionalized mesoporous silica and Nafion composite electrodes. *Anal. Chim. Acta* **2008**, *620*, 55-63.

52. Guell, R.; Aragay, G.; Fontas, C.; Antico, E.; Merkoci, A. Sensitive and stable monitoring of lead and cadmium in seawater using screen-printed electrode and electrochemical stripping analysis. *Anal. Chim. Acta* **2008**, *627*, 219-224.

53. Bagal-Kestwal, D.; Karve, M.S.; Kakade, B.; Pillai, V.K. Invertase inhibition based electrochemical sensor for the detection of heavy metal ions in aqueous system: Application of ultra-microelectrode to enhance sucrose biosensor's sensitivity. *Biosens. Bioelectron.* **2008**, *24*, 657-664.

54. Rico, M.A.G.; Olivares-Marin, M.; Gil, E.P. Modification of carbon screen-printed electrodes by adsorption of chemically synthesized Bi nanoparticles for the voltammetric stripping detection of Zn(II), Cd(II) and Pb(II). *Talanta* **2009**, *80*, 631-635.

55. Cooper, J.; Bolbot, J.A.; Saini, S.; Setford, S.J. Electrochemical method for the rapid on site screening of cadmium and lead in soil and water samples. *Water Air Soil Poll.* **2007**, *179*, 183-195.

56. Zou, Z.W.; Jang, A.; MacKnight, E.; Wu, P.M.; Do, J.; Bishop, P.L.; Ahn, C.H. Environmentally friendly disposable sensors with microfabricated on-chip planar bismuth electrode for *in situ* heavy metal ions measurement. *Sensor. Actuat. B-Chem.* **2008**, *134*, 18-24.

57. Kadara, R.O.; Tothill, I.E. Development of disposable bulk-modified screen-printed electrode based on bismuth oxide for stripping chronopotentiometric analysis of lead(II) and cadmium(II) in soil and water samples. *Anal. Chim. Acta* **2008**, *623*, 76-81.

58. Lee, H.J.; Lagger, G.; Pereira, C.M.; Silva, A.F.; Girault, H.H. Amperometric tape ion sensors for cadmium(II) ion analysis. *Talanta* **2009**, *78*, 66-70.

59. Toghill, K.E.; Xiao, L.; Wildgoose, G.G.; Compton, R.G. Electroanalytical Determination of Cadmium(II) and Lead(II) Using an Antimony Nanoparticle Modified Boron-Doped Diamond Electrode. *Electroanal.* **2009**, *21*, 1113-1118.

60. Ensafi, A.A.; Meghdadi, S.; Sedighi, S. Sensitive cadmium potentiometric sensor based on 4-hydroxy salophen as a fast tool for water samples analysis. *Desalination* **2009**, *242*, 336-345.

61. Gupta, V.K.; Jain, A.K.; Ludwig, R.; Maheshwari, G. Electroanalytical studies on cadmium(II) selective potentiometric sensors based on t-butyl thiacalix[4]arene and thiacalix[4]arene in poly(vinyl chloride). *Electrochim. Acta* **2008**, *53*, 2362-2368.

62. Berezhetskyy, A.L.; Sosovska, O.F.; Durrieu, C.; Chovelon, J.M.; Dzyadevych, S.V.; Tran-Minh, C. Alkaline phosphatase conductometric biosensor for heavy-metal ions determination. *Innov. Tech. Biol. Med. RBM* **2008**, *29*, 136-140.

63. Ensafi, A.A.; Meghdadi, S.; Fooladgar, E. Development of a new selective optical sensor for Cd(II) Ions based on 4-Hydroxy Salophen. *IEEE Sens. J.* **2008**, *8*, 1794-1800.

64. Luo, H.Y.; Jiang, J.H.; Zhang, X.B.; Li, C.Y.; Shen, G.L.; Yu, R.Q. Synthesis of porphyrin-appended terpyridine as a chemosensor for cadmium based on fluorescent enhancement. *Talanta* **2007**, *72*, 575-581.
65. Wang, Z.; Palacios, M.A.; Anzenbacher, P. Fluorescence sensor array for metal ion detection based on various coordination chemistries: General performance and potential application. Anal. Chem. 2008, 80, 7451-7459.

66. Banerjee, S.; Kara, S.; Santra, S. A simple strategy for quantum dot assisted selective detection of cadmium ions. Chem. Commun. 2008, 3037-3039.

67. Tang, X.L.; Peng, X.H.; Dou, W.; Mao, J.; Zheng, J.R.; Qin, W.W.; Liu, W.S.; Chang, J.; Yao, X.J. Design of a semirigid molecule as a selective fluorescent chemosensor for recognition of Cd(II). Org. Lett. 2008, 10, 3653-3656.

68. INERIS Cadmium et ses dérivés; INERIS: 22/02/2005, 2005; p 60.

69. Dittman, J.A.; Shanley, J.B.; Driscoll, C.T.; Aiken, G.R.; Chalmers, A.T.; Towse, J.E. Ultraviolet absorbance as a proxy for total dissolved mercury in streams. Environ. Pollut. 2009, 157, 1953-1956.

70. Lee, J.S.; Mirkin, C.A. Chip-based scanometric detection of mercuric ion using DNA-functionalized gold nanoparticles. Anal. Chem. 2008, 80, 6805-6808.

71. Amini, M.K.; Khezri, B.; Firooz, A.R. Development of a highly sensitive and selective optical chemical sensor for batch and flow-through determination of mercury ion. Sensor. Actuat. B-Chem. 2008, 131, 470-478.

72. Yari, A.; Papi, F. Highly selective sensing of mercury(II) by development and characterization of a PVC-based optical sensor. Sensor. Actuat. B-Chem. 2009, 138, 467-473.

73. Khezri, B.; Amini, M.K.; Firooz, A.R. An optical chemical sensor for mercury ion based on 2-mercaptopyrimidine in PVC membrane. Anal. Bioanal. Chem. 2008, 1-8.

74. Li, J.S.; Yao, J.J.; Zhong, W.W. Membrane blotting for rapid detection of mercury(II) in water. Chem. Commun. 2009, 33, 4962-4964.

75. Kalyan, Y.; Pandey, A.K.; Bhagat, P.R.; Acharya, R.; Natarajan, V.; Naidu, G.R.K.; Reddy, A.V.R. Membrane optode for mercury(II) determination in aqueous samples. J. Hazard. Mater. 2009, 166, 377-382.

76. El-Safty, S.A., Organic-inorganic hybrid mesoporous monoliths for selective discrimination and sensitive removal of toxic mercury ions. J. Mater. Sci. 2009, 44, 6764-6774.

77. Shunmugam, R.; Gabriel, G.J.; Smith, C.E.; Aamer, K.A.; Tew, G.N. A highly selective colorimetric aqueous sensor for mercury. Chem.Eur. J. 2008, 14, 3904-3907.

78. Shao, N.; Gao, X.; Wang, H.; Yang, R.H.; Chan, W.H. Spiropyran-based optical approaches for mercury ion sensing: Improving sensitivity and selectivity via cooperative ligation interactions using cysteine. Anal. Chim. Acta 2009, 655, 1-7.

79. Ensafi, A.A.; Katiraei Far, A.; Meghdadi, S. Highly selective optical sensor for mercury assay based on covalent immobilization of 4-hydroxy salophen on a triacetylcellulose membrane. Sensor. Actuat. B-Chem. 2008, 133, 84-90.

80. Ensafi, A.A.; Fouladgar, M. A sensitive and selective bulk optode for determination of Hg(II) based on hexathiacyclooctadecane and chromoionophore V. Sensor. Actuat. B-Chem. 2009, 136, 326-331.

81. Ros-Lis, J.V.; Casasús, R.; Comes, M.; Coll, C.; Marcos, M.D.; Martínez-Máñez, R.; Sancenón, F.; Soto, J.; Amorós, P.; El Haskouri, J.; Garró, N.; Rurack, K. A Mesoporous 3D Hybrid Material with Dual Functionality for Hg^{2+} Detection and Adsorption. Chem.Eur. J. 2008, 14, 8267-8278.
82. Ensafi, A.A.; Fouladgar, M. Development of a spectrophotometric optode for the determination of Hg(II). IEEE Sens. J. 2008, 8, 347-353.
83. Leng, B.; Zou, L.; Jiang, J.; Tian, H. Colorimetric detection of mercuric ion (Hg$^{2+}$) in aqueous media using chemodosimeter-functionalized gold nanoparticles. Sensor. Actuat. B-Chem. 2009, 140, 162-169.
84. Nuriman; Kuswandi, B.; Verboom, W. Selective chemosensor for Hg(II) ions based on tris[2-(4-phenyldiazenyl)phenylaminoethoxy]cyclotriveratrylene in aqueous samples. Anal. Chim. Acta 2009, 655, 75-79.
85. Pérez-Hernández, J.; Albero, J.; Llobet, E.; Correig, X.; Matías, I.R.; Arregui, F.J.; Palomares, E. Mercury optical fibre probe based on a modified cladding of sensitised Al$_2$O$_3$ nano-particles. Sensor. Actuat. B-Chem. 2009, 143, 103-110.
86. Lee, S.J.; Lee, J.E.; Seo, J.; Jeong, I.Y.; Lee, S.S.; Jung, J.H. Optical sensor based on nanomaterial for the selective detection of toxic metal ions. Adv. Funct. Mater. 2007, 17, 3441-3446.
87. Zheng, A.F.; Chen, J.L.; Wu, G.N.; Wei, H.P.; He, C.Y.; Kai, X.M.; Wu, G.H.; Chen, Y.C. Optimization of a sensitive method for the “switch-on” determination of mercury(II) in waters using Rhodamine B capped gold nanoparticles as a fluorescence sensor. Microchim. Acta 2009, 164, 17-27.
88. Ye, B.C.; Yin, B.C. Highly Sensitive Detection of Mercury(II) Ions by Fluorescence Polarization Enhanced by Gold Nanoparticles. Angew. Chem. Int. Edit. 2008, 47, 8386-8389.
89. Huang, W.; Zhou, P.; Yan, W.B.; He, C.; Xiong, L.Q.; Li, F.Y.; Duan, C.Y. A bright water-compatible sugar-rhodamine fluorescence sensor for selective detection of Hg$^{2+}$ in natural water and living cells. J. Environ. Monitor. 2009, 11, 330-335.
90. Liu, C.W.; Huang, C.C.; Chang, H.T. Highly Selective DNA-Based Sensor for Lead(II) and Mercury(II) Ions. Anal. Chem. 2009, 81, 2383-2387.
91. He, C.S.; Zhu, W.P.; Xu, Y.F.; Chen, T.; Qian, X.H. Trace mercury(II) detection and separation in serum and water samples using a reusable bifunctional fluorescent sensor. Anal. Chim. Acta 2009, 651, 227-233.
92. Yu, C.J.; Cheng, T.L.; Tseng, W.L. Effects of Mn$^{2+}$ on oligonucleotide-gold nanoparticle hybrids for colorimetric sensing of Hg$^{2+}$: Improving colorimetric sensitivity and accelerating color change. Biosens. Bioelectron. 2009, 25, 204-210.
93. Guo, L.Q.; Hu, H.; Sun, R.Q.; Chen, G.A. Highly sensitive fluorescent sensor for mercury ion based on photoinduced charge transfer between fluorophore and pi-stacked T-Hg(II)-T base pairs. Talanta 2009, 79, 775-779.
94. Han, Z.X.; Luo, H.Y.; Zhang, X.B.; Kong, R.M.; Shen, G.L.; Yu, R.Q. A ratiometric chemosensor for fluorescent determination of Hg$^{2+}$ based on a new porphyrin-quinoline dyad. Spectrochim. Acta A 2009, 72, 1084-1088.
95. Ren, X.; Xu, Q.H. Highly sensitive and selective detection of mercury ions by using oligonucleotides, DNA intercalators, and conjugated polymers. Langmuir 2009, 25, 29-31.
96. Long, F.; He, M.; Shi, H.C.; Zhu, A.N. Development of evanescent wave all-fiber immunosensor for environmental water analysis. Biosens. Bioelectron. 2008, 23, 952-958.
97. Yang, Y.; Jiang, J.; Shen, G.; Yu, R. An optical sensor for mercury ion based on the fluorescence quenching of tetra(p-dimethylaminophenyl)porphyrin. *Anal. Chim. Acta* **2009**, *636*, 83-88.

98. Liu, X.; Tang, Y.; Wang, L.; Zhang, J.; Song, S.; Fan, C.; Wang, S. Optical detection of mercury(II) in aqueous solutions by using conjugated polymers and label-free oligonucleotides. *Adv. Mater.* **2007**, *19*, 1471-1474.

99. Liu, C.W.; Huang, C.C.; Chang, H.T. Control over surface DNA density on gold nanoparticles allows selective and sensitive detection of mercury(II). *Langmuir* **2008**, *24*, 8346-8350.

100. Nolan, E.M.; Lippard, S.J. Turn-on and ratiometric mercury sensing in water with a red-emitting probe. *J. Am. Chem. Soc.* **2007**, *129*, 5910-5918.

101. Lee, D.N.; Kim, G.J.; Kim, H.J. A fluorescent coumarinylalkyne probe for the selective detection of mercury(II) ion in water. *Tetrahedron Lett.* **2009**, *50*, 4766-4768.

102. Wanichacheva, N.; Siriprumpoonthum, M.; Kamkaew, A.; Grudpan, K. Dual optical detection of a novel selective mercury sensor based on 7-nitrobenzo-2-oxa-1,3-diazolyl subunits. *Tetrahedron Lett.* **2009**, *50*, 1783-1786.

103. Li, C.Y.; Zhang, X.B.; Qiao, L.; Zhao, Y.; He, C.M.; Huan, S. Y.; Lu, L.M.; Jian, L.X.; Shen, G.L.; Yu, R.Q. Naphthalimide-Porphyrin hybrid based ratiometric bioimaging probe for Hg$^{2+}$: well-resolved emission spectra and unique specificity. *Anal. Chem.* **2009**, *81*, 9993-10001.

104. Li, H.; Yan, H. Ratiometric fluorescent mercuric sensor based on thiourea-thiadiazole- pyridine linked organic nanoparticles. *J. Phys. Chem. C* **2009**, *113*, 7526-7530.

105. Shang, Z.B.; Wang, Y.; Jin, W.J. Triethanolamine-capped CdSe quantum dots as fluorescent sensors for reciprocal recognition of mercury (II) and iodide in aqueous solution. *Talanta* **2009**, *78*, 364-369.

106. Liu, Y.; Yu, M.; Chen, Y.; Zhang, N. Convenient and highly effective fluorescence sensing for Hg$^{2+}$ in aqueous solution and thin film. *Bioorg. Med. Chem.* **2009**, *17*, 3887-3891.

107. Wang, J.; Huang, L.; Xue, M.; Liu, L.; Wang, Y.; Gao, L.; Zhu, J.; Zou, Z. Developing a novel fluorescence chemosensor by self-assembly of Bis-Schiff base within the channel of mesoporous SBA-15 for sensitive detecting of Hg$^{2+}$ ions. *Appl. Surf. Sci.* **2008**, *254*, 5329-5335.

108. Vaswani, K.G.; Keranen, M.D. Detection of aqueous mercuric ion with a structurally simple 8-hydroxyquinoline derived ON-OFF fluorosensor. *Inorg. Chem.* **2009**, *48*, 5797-5800.

109. Ivask, A.; Green, T.; Polyak, B.; Mor, A.; Kahru, A.; Virta, M.; Marks, R. Fibre-optic bacterial biosensors and their application for the analysis of bioavailable Hg and As in soils and sediments from Aznalcollar mining area in Spain. *Biosens. Bioelectron.* **2007**, *22*, 1396-1402.

110. Kanan, S.M.; Abu-Yousef, I.A.; Hassouneh, N.; Malkawi, A.; Abdo, N.; Kanan, M.C. A highly selective luminescent sensor for detecting mercuric ions in water. *Aust. J. Chem.* **2009**, *62*, 1593-1599.

111. Kong, R.M.; Zhang, X.B.; Zhang, L.L.; Jin, X.Y.; Huan, S.Y.; Shen, G.L.; Yu, R.Q. An ultrasensitive electrochemical “turn-on” label-free biosensor for Hg$^{2+}$ with AuNP-functionalized reporter DNA as a signal amplifier. *Chem. Commun.* **2009**, *5633-5635.

112. Seehra, M.S.; Ranganathan, S.; Manivannan, A. Electrochemical quantification of mercury in solutions using boron-doped diamond electrodes: Electrode regeneration and role of gold and impurities. *Anal. Lett.* **2008**, *41*, 2162-2170.
113. Khadro, B.; Vittori, O.; Jaffreziec-Renault, N. A new differential pulse anodic stripping voltammetry miniaturized sensor system for detection of nickel and mercury in waters. *Sens. Lett.* **2009**, *7*, 829-832.

114. Kim, T.H.; Lee, J.; Hong, S. Highly selective environmental nanosensors based on anomalous response of carbon nanotube conductance to mercury ions. *J. Phys. Chem-C* **2009**, *113*, 19393-19396.

115. Gupta, V.K.; Singh, A.K.; Al Khayat, A.; Gupta, B. Neutral carriers based polymeric membrane electrodes for selective determination of mercury(II). *Anal. Chim. Acta* **2007**, *590*, 81-90.

116. Şar, E.; Berber, H.; Aşçı, B.; Cankıtrtaran, H. Determination of some heavy metal ions with a carbon paste electrode modified by poly(glycidylmethacrylate-methylmethacrylate-divinylbenzene) microspheres functionalized by 2-aminothiazole. *Electroanal.* **2008**, *20*, 1533-1541.

117. Javanbakht, M.; Divsar, F.; Badiei, A.; Ganjali, M.R.; Norouzi, P.; Ziarani, G.M.; Chalooei, M.; Jahangir, A.A. Potentiometric detection of Mercury(II) ions using a carbon paste electrode modified with substituted thiourea-functionalized highly ordered nanoporous Silica. *Anal. Sci.* **2009**, *25*, 789-794.

118. Han, D.; Kim, Y.R.; Oh, J.W.; Kim, T.H.; Mahajan, R.K.; Kim, J.S.; Kim, H. A regenerative electrochemical sensor based on oligonucleotide for the selective determination of mercury(II). *Analyst* **2009**, *134*, 1857-1862.

119. Ensafi, A.A.; Meghdadi, S.; Allafchian, A.R. Highly selective potentiometric membrane sensor for Hg(II) based on bis(benzoyl acetone) diethylene triamine. *IEEE Sens. J.* **2008**, *8*, 248-254.

120. Abu-Shawish, H.M. A mercury(II) selective sensor based on N,N'-bis(salicylaldehyde)-phenylenediamine as neutral carrier for potentiometric analysis in water samples. *J. Hazard. Mater.* **2009**, *167*, 602-608.

121. Khun, N.W.; Liu, E. Linear sweep anodic stripping voltammetry of heavy metals from nitrogen doped tetrahedral amorphous carbon thin films. *Electrochim. Acta* **2009**, *54*, 2890-2898.

122. Marcolino-Junior, L.H.; Janegitz, B.C.; Lourenção, B.C.; Fatibello-Filho, O. Anodic stripping voltammetric determination of mercury in water using a chitosan-modified carbon paste electrode. *Anal. Lett.* **2007**, *40*, 3119-3128.

123. Guascito, M.R.; Malitesta, C.; Mazzotta, E.; Turco, A. Inhibitive determination of metal ions by an amperometric glucose oxidase biosensor—Study of the effect of hydrogen peroxide decomposition. *Sensor. Actuat. B-Chem.* **2008**, *131*, 394-402.

124. Kokkinos, C.; Economou, A.; Raptis, I.; Speliotis, T. Disposable mercury-free cell-on-a-chip devices with integrated microfabricated electrodes for the determination of trace nickel(II) by adsorptive stripping voltammetry. *Anal. Chim. Acta* **2008**, *622*, 111-118.

125. Li, H.B.; Cui, Z.M.; Han, C.P. Glutathione-stabilized silver nanoparticles as colorimetric sensor for Ni$^{2+}$ ion. *Sensor. Actuat. B-Chem.* **2009**, *143*, 87-92.

126. El Mhammedi, M.A.; Achak, M.; Chtaini, A. Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ modified carbon-paste electrode for the determination of trace lead(II) by square-wave voltammetry. *J. Hazard. Mater.* **2009**, *161*, 55-61.
127. Nasraoui, R.; Floner, D.; Geneste, F. Analytical performances of a flow electrochemical sensor for preconcentration and stripping voltammetry of metal ions. *J. Electroanal. Chem.* 2009, 629, 30-34.

128. Faridbod, F.; Ganjali, M.R.; Larijani, B.; Hosseini, M.; Alizadeh, K.; Norouzi, P. Highly selective and sensitive asymmetric lead microsensor based on 5,5′-dithiobis(2-nitrobenzoic acid) as an excellent hydrophobic neutral carrier for nano level monitoring of lead in real samples. *Int. J. Electrochem. Sc.* 2009, 4, 1528-1540.

129. Turek, M.; Heiden, W.; Riesen, A.; Chhabda, T.A.; Schubert, J.; Zander, W.; Krüger, P.; Keusgen, M.; Schöning, M.J. Artificial intelligence/fuzzy logic method for analysis of combined signals from heavy metal chemical sensors. *Electrochim. Acta* 2009, 54, 6082-6088.

130. Hassan, R.Y.A.; Habib, I.H.I.; Hassan, H.N.A. Voltammetric determination of lead (II) in medical lotion and biological samples using chitosan-carbon paste electrode. *Int. J. Electrochem. Sc.* 2008, 3, 935-945.

131. Vedhi, C.; Selvanathan, G.; Arumugam, P.; Manisankar, P. Electrochemical sensors of heavy metals using novel polymer-modified glassy carbon electrodes. *Ionics* 2008, 1-7.

132. Yantasee, W.; Hongsirikarn, K.; Warner, C.L.; Choi, D.; Sangvanich, T.; Toloczko, M.B.; Warner, M.G.; Fryxell, G.E.; Addleman, R.S.; Timchalk, C. Direct detection of Pb in urine and Cd, Pb, Cu, and Ag in natural waters using electrochemical sensors immobilized with DMSA functionalized magnetic nanoparticles. *Analyst* 2008, 133, 348-355.

133. Li, X.G.; Ma, X.L.; Huang, M.R. Lead(II) ion-selective electrode based on polyaminoanthraquinone particles with intrinsic conductivity. *Talanta* 2009, 78, 498-505.

134. Kazemi, S.Y.; Shamsipur, M.; Sharghi, H. Lead-selective poly(vinyl chloride) electrodes based on some synthesized benzo-substituted macrocyclic diamides. *J. Hazard. Mater.* 2009, 172, 68-73.

135. Zuo, P.; Yin, B.C.; Ye, B.C. DNAzyme-based microarray for highly sensitive determination of metal ions. *Biosens. Bioelectron.* 2009, 25, 935-939.

136. Ensafi, A.A.; Far, A.K.; Meghdadi, S. Highly selective optical-sensing film for lead(II) determination in water samples. *J. Hazard. Mater.* 2009, 172, 1069-1075.

137. Yu, M.; He, F.; Tang, Y.; Wang, S.; Li, Y.; Zhu, D. Non-ionic water-soluble crown-ether-substituted polyfluorene as fluorescent probe for lead ion assays. *Macromol. Rapid Commun.* 2007, 28, 1333-1338.

138. Ensafi, A.A.; Fouladgar, M. Development a simple PVC membrane bulk optode for determination of lead ions in water samples. *Sens. Lett.* 2009, 7, 177-184.

139. Cauchi, M.; Bessant, C.; Setford, S. Simultaneous Quantitative Determination of cadmium, lead, and copper on carbon-ink screen-printed electrodes by differential pulse anodic stripping voltammetry and partial least squares regression. *Electroanal.* 2008, 20, 2571-2577.

140. Pardieu, E.; Cheap, H.; Vedrine, C.; Lazerges, M.; Lattach, Y.; Garnier, F.; Ramita, S.; Pernelle, C. Molecularly imprinted conducting polymer based electrochemical sensor for detection of atrazine. *Anal. Chim. Acta* 2009, 649, 236-245.

141. Farré, M.; Martinez, E.; Ramon, J.; Navarro, A.; Radjenovic, J.; Mauriz, E.; Lechuga, L.; Marco, M.P.; Barcelo, D. Part per trillion determination of atrazine in natural water samples by a surface plasmon resonance immunosensor. *Anal. Bioanal. Chem.* 2007, 388, 207-214.
142. Vervllet-Scheebaurn, M.; Ritzenthaler, R.; Normann, J.; Wagner, E. Short-term effects of benzalkonium chloride and atrazine on *Elodea canadensis* using a miniaturised microbioreactor system for an online monitoring of physiologic parameters. *Ecotox. Environ. Safe.* 2008, 69, 254-262.

143. Gouzy, M.F.; Keß, M.; Krämer, P.M. A SPR-based immunosensor for the detection of isoproturon. *Biosens. Bioelectron.* 2009, 24, 1563-1568.

144. Lee, D.Y.; Kang, H.W.; Kaneko, S.; Kwon, Y.S.; Muramatsu, H. Direct monitoring of paraquat induced cell death using quartz crystal sensor. *Thin Solid Films* 2009, 518, 707-710.

145. Mauriz, E.; Calle, A.; Manclús, J.J.; Montoya, A.; Hildebrandt, A.; Barcelo, D.; Lechuga, L.M. Optical immunosensor for fast and sensitive detection of DDT and related compounds in river water samples. *Biosens. Bioelectron.* 2007, 22, 1410-1418.

146. Lisha, K.P.; Anshup; Pradeep, T. Enhanced visual detection of pesticides using gold nanoparticles. *J. Environ. Sci. Heal. B* 2009, 44, 697-705.

147. Zhao, W.; Ge, P.Y.; Xu, J.J.; Chen, H.Y. Selective detection of hypertoxic organophosphates pesticides via PDMS composite based acetylcholinesterase-inhibition biosensor. *Environ. Sci. Technol.* 2009, 43, 6724-6729.

148. Yin, H.S.; Ai, S.Y.; Xu, J.; Shi, W.J.; Zhu, L.S. Amperometric biosensor based on immobilized acetylcholinesterase on gold nanoparticles and silk fibroin modified platinum electrode for detection of methyl paraoxon, carbofuran and phoxim. *J. Electroanal. Chem.* 2009, 637, 21-27.

149. Mensah-Brown, A.K.; Wenzel, M.J.; Josse, F.J.; Yaz, E.E. Near real-time monitoring of organophosphate pesticides in the aqueous-phase using SH-SAW sensors Including Estimation-Based Signal Analysis. *IEEE Sens. J.* 2009, 9, 1817-1824.

150. Khenifi, A.; Derriche, Z.; Forano, C.; Prevot, V.; Mosty, C.; Scavetta, E.; Ballarin, B.; Guadagnini, L.; Tonelli, D. Glyphosate and glufosinate detection at electrogenerated NiAl-LDH thin films. *Anal. Chim. Acta* 2009, 654, 97-102.

151. Hildebrandt, A.; Ribas, J.; Bragos, R.; Marty, J.L.; Tresanchez, M.; Lacorte, S. Development of a portable biosensor for screening neurotoxic agents in water samples. *Talanta* 2008, 75, 1208-1213.

152. Hildebrandt, A.; Bragos, R.; Lacorte, S.; Marty, J.L. Performance of a portable biosensor for the analysis of organophosphorus and carbamate insecticides in water and food. *Sensor. Actuat. B-Chem.* 2008, 133, 195-201.

153. Wang, Z.G., Electrochemical Investigation of Methyl Parathion at a Poly-L-cysteine Film-modified Glassy Carbon Electrode. *Chem. Anal. (Warsaw, Pol.)* 2009, 54, 403-414.

154. Gong, J.M.; Liu, T.; Song, D.D.; Zhang, X.B.; Zhang, L.Z. One-step fabrication of three-dimensional porous calcium carbonate-chitosan composite film as the immobilization matrix of acetylcholinesterase and its biosensing on pesticide. *Electrochem. Commun.* 2009, 11, 1873-1876.

155. Shimomura, T.; Itoh, T.; Sumiya, T.; Mizukami, F.; Ono, M. Amperometric biosensor based on enzymes immobilized in hybrid mesoporous membranes for the determination of acetylcholine. *Enzyme Microb. Tech.* 2009, 45, 443-448.
156. Upadhyay, S.; Rao, G.R.; Sharma, M.K.; Bhattacharya, B.K.; Rao, V.K.; Vijayaraghavan, R. Immobilization of acetylcholineesterase-choline oxidase on a gold-platinum bimetallic nanoparticles modified glassy carbon electrode for the sensitive detection of organophosphate pesticides, carbamates and nerve agents. *Biosens. Bioelectron.* 2009, 25, 832-838.

157. Yang, X.F.; Lin, L.; Sun, D. Electrochemical behaviors and analysis of parathion at nano-alumina film modified electrode. *Chin. J. Anal. Chem.* 2009, 37, 1057-1060.

158. Du, D.; Wang, J.; Smith, J.N.; Timchalk, C.; Lin, Y.H. Biomonitoring of organophosphorus agent exposure by reactivation of cholinesterase enzyme based on carbon nanotube-enhanced flow-injection amperometric detection. *Anal. Chem.* 2009, 81, 9314-9320.

159. Lima, K.M.G.; Raimundo Jr, I.M.; Pimentel, M.F. Improving the detection limits of near infrared spectroscopy in the determination of aromatic hydrocarbons in water employing a silicone sensing phase. *Sensor. Actuat. B-Chem.* 2007, 125, 229-233.

160. Silva, A.M.S.; Pimentel, M.F.; Raimundo Jr, I.M.; Almeida, Y.M.B. A PVC sensing phase for determination of BTEX in water employing mid-infrared spectroscopy. *Vib. Spectrosc.* 2008, 46, 39-44.

161. Carvalho, E.R.; Correa, A.A.; Filho, N.C.; Oliveira Jr., O.N.; Gomes, H.L.; Mattoso, L.H.C.; Martin-Neto, L. Detection of chloroform with a sensor array consisting of electrochemically deposited polythiophenes films: Processes governing the electrical response. *Sens. Lett.* 2007, 5, 374-379.

162. Kurup, P.U. Novel technologies for sniffing soil and ground water contaminants. *Curr. Sci. India* 2009, 97, 1212-1219.

© 2010 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/3.0/).