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MICROFLUIDICS AND MATERIALS FOR SMART WATER MONITORING: A REVIEW

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Keywords: Microfluidic; water monitoring; functional material; environment; Lab on a Chip

Abstract

Water quality monitoring of drinking, waste, continental and seawaters is of great importance to ensure safety and wellbeing for humans, fauna and flora. Researchers are developing robust water monitoring microfluidic devices but, the delivery of a cost-effective, commercially available platform has not been achieved yet. Conventional water monitoring is mainly based on laboratory instruments or on sophisticated and expensive handheld probes for on-site analysis, both requiring trained personnel and being time-consuming. As an alternative, microfluidics has emerged as a powerful tool with the capacity to displace conventional analytical systems. Nevertheless, microfluidic devices largely use conventional pumps and valves for operation, and

electronics for sensing, that increment the dimensions and costs of the final platforms, diminishing their commercialization perspectives. In this review, we critically analyze the characteristics of conventional microfluidic devices for water monitoring, focusing on different water matrices (drinking, waste, continental and seawaters), towards their application in potential commercial products. Moreover, we introduce the revolutionary concept of using functional materials such as hydrogels, poly(ionic liquid) hydrogels and ionogels as alternatives to conventional fluidic handling and sensing tools for water monitoring in microfluidic devices.

1. Introduction

Water security is recognized as one of the great challenges of the 21st century by many international organizations. For instance, the World's Health Organization (WHO) sets water quality assessment as a top global priority, being safe water supplies for drinking and recreation, hygienic sanitation and good water management fundamental for human health [1]. Unfortunately, water pollution and water-related diseases have dreadful consequences in the body [2] such as diarrhoea, which is killing around 900.000 people every year in developing countries with no access to proper water infrastructures [1,3,4]. Moreover, environmentally speaking, alterations in the nutrients and oxygen balance can result in eutrophication, the uncontrolled growth of plants or algae in water bodies [5].

Therefore, continuous monitoring of water resources such as continental water seawater and in particular, wastewater and drinking water, for human and animal consumption, is essential [6]. In order to do that, physico-chemical parameters such as temperature, pH, salinity, oxygen balance, acid neutralising capacity, and nutrient concentrations (nitrates and nitrites, phosphates, ammonium, silicates, sulphates, etc.) need to be monitored, and necessary controlled, in order to guarantee optimal water quality [7]. Traditionally, water samples are collected at the point of need, by trained personnel, and transported to specialized analytical laboratories for quality control [8-14]. Advantages of laboratory-based methods include the possibility to analyze many samples with high accuracy and precision, obtaining low limits of detection and quantification, with automated equipment. Their main disadvantage is that, in general, this equipment is not portable, therefore neglecting *in situ* analysis, potentially compromising sample's stability. Economically speaking, these kind of

equipment are normally very expensive and require trained personnel to prepare and handle the samples. This type of technology is evolving continuously, generating more compact, ease to use and cheap equipment to be operated at conventional laboratory facilities. This is the case of portable kits, that allow on-site testing, becoming very useful when resources are limited, as they are fast and simple to use and at the same time inexpensive. On the bad side, these kits require trained personnel and do not offer accurate results, since provide with an estimation of water composition thus, does not fully meet user needs [15]. As an alternative to portable kits, water quality analysis probes have been developed and commercialized. The main advantage of these devices, together with their portability, is their high accuracy. Nevertheless, they are not affordable by any type of budgets due to their elevated costs and the need manual intervention during data collection. The most advanced versions integrate wireless sensor networks where data can be collected and delivered through internet [16].

The natural evolution of this technology presents a future where humanity will make use of effective deployable autonomous sensors in lakes and rivers, water supply systems and even connected to municipal and industrial wastewater treatment plants, for accurate and precise water monitoring at the point of need. Furthermore, the information will be made available to citizens through Internet. Potentially, these sensors will be even made wearable, where the wearer becomes the sensor, able to monitor his/her surrounding water environment.

Despite the huge efforts to develop innovative sensors [17], the current state-of-the-art for autonomous environmental devices to monitor the chemical and biological status of our water resources is based on autonomous flow systems [18] that employ conventional pumps, valves and fluid handling components, and because of this, these systems are usually expensive (often > €20K per unit). Therefore, the goal is to generate autonomous devices that integrate all necessary steps for a defined (bio)-chemical analysis such as sampling, sample transport, filtration, dilution, chemical reaction, separation and detection without the need of conventional components. This concept is called micro Total Analysis System (μ TAS) [19]. Indeed, a μ TAS or a lab-on-a-chip (LOC) has the ambition of shrinking an entire laboratory to a chip format. Reviewers stated that LOC and electrochemical sensing-based portable monitoring systems are good alternatives to conventional methods [6] and present the advances

and shortcomings of different methodologies in microfluidic-based sensors for water quality monitoring [2]. In particular, two main aspects are rapidly developing and adapting to the new needs on water monitoring:

- (1) the engineering of the equipment used for analysis both in lab and in field, that has evolved to the miniaturization of the devices and to the incorporation of more precise detection technologies for the creation of integrated systems. These systems have experienced the evolution from simple sampling and handling to more complex automated sampling units that allow higher control and larger number of samples to be analyzed [20]. A major benefactor to this evolution has been microfluidic technology, which permits fast and cheap analysis of samples, on-site and with low reagent consumption [21]. This novel formatting saves protocols time, reduces risk of sample losses or contaminations and reduces costs by avoiding the use of bulky expensive laboratory instrumentation. Furthermore, microfluidics allows for full automation, thus increasing throughput, improving ease of use and repeatability by reducing human errors.
- (2) the use of novel materials, like functional materials for sensing, where ingenious uses of structured materials [22-24], under controlled laboratory conditions, exhibit greatly improved characteristics compared to conventional sensors. Therefore, these new types of sensors have the potential to improve environmental analysis systems.

However, despite these exciting developments, there is rarely found any example of these type of systems being used in real deployment sites. Nevertheless, the key to change the current model is to drive down the costs per unit, making autonomous environmental devices available for €500 or even €20. It is capital to be able to develop integrable microfluidic sensors and actuators, fabricated through innovative breakthroughs emerging from fundamental materials science research. They should be fabricated at a reasonable price by using scalable fabrication techniques, compatible with mass production and commercialization, reducing device dimensions without losing any of the advantages of existing technology [25]. (Figure 1).

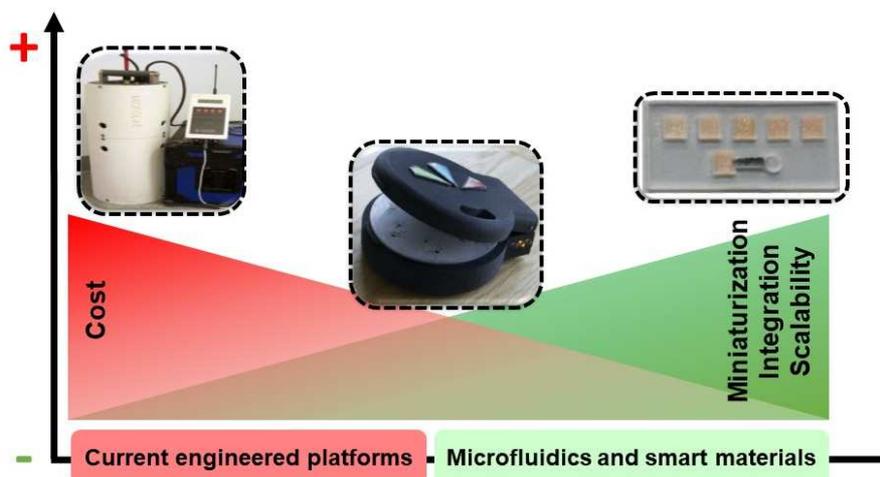


Figure 1: Schematic strategy used in this review. Pictures in bubbles are developed platforms for water monitoring (left: multianalysis commercial probe; center: hand held system based on a centrifugal microfluidic device [26]; right: Point-of-Need microfluidic device [27]. (1) Current platforms are expensive and bulky whereas difficult to miniaturize and integrate to meet scalability. (2) Truly scalable device developed comes through the integration of innovative breakthroughs in materials research and microfluidics.

This review summarises the current state-of-the-art in autonomous microfluidic devices and systems for environmental water monitoring, focusing on different water matrices such as drinking water, wastewater, continental waters (rivers, lakes ...) and seawater. Moreover, the review will set a material science perspective, where the integration of functional materials, as alternatives to conventional fluidic handling and sensing building blocks is capital to reach devices commercialization.

2. Microfluidic Devices for Water Monitoring

Microfluidic devices provide a way to perform analysis in remote locations, enabling *in situ* analysis at the Point-of-Need [28]. Reduced measurement times, improvements in sensitivity, enhancement of selectivity and high repeatability are advantages of microfluidic devices when integrated in μ TAS [29]. Despite the huge efforts of researchers on providing fully integrated, portable and feasible platforms for environmental sensing, μ TAS are hardly used in commercial products. There are several examples that have reached the market, such as the 2100 Bioanalyzer of Agilent Technologies, micromixers and microreactors from Micronit, and multiflux by

Dolomite, but are mainly focused on Point-of-Care diagnostics [30]. Moreover, to the best of our knowledge they are not commercial examples of this type of technology used in integrated or standardized analytical processes for water monitoring.

In 2010, Royce W. Murray highlighted that the analytical chemistry community is facing the challenge to develop environmental platforms for water monitoring [31]. Nowadays, these platforms are becoming available through microfluidics but are still struggling to deliver reliable platforms. George Whitesides referred to this issue in 2014 stating that “LOC technology is now shifting from fundamental areas to serious explorations of uses and to demonstrations and applications with real potential to provide the incentive for further and more extensive industrial engineering development, and ultimately to incorporation into products” [32]. Today, the industrial engineer step is a reality as it is possible to produce, at high scale, microfluidic technology. The next step is to merge the knowledge coming from research with the needs from industry, to translate this technology into a commercial success [33].

Over the last few years microfluidic devices and platforms have been delivered for the monitoring of pollutants in a variety of water matrices: drinking water, waste and sewage waters, continental water (rivers, lakes, ...), and seawater. Drinking water devices are normally fabricated to suit pathogens and bacteria detection. In contrast, waste and sewage, continental water and seawater devices need to be deployable for long periods of time, under drastic environmental conditions. There are many reviews available on a wider perspective of microfluidic technology for environmental monitoring [2,18] but none of them summarized the existing technology for different water matrices.

In the following sections, the state-of-the-art on deployable microfluidic devices and field-deployable microfluidic systems for *in situ* chemical analysis in different water matrices will be reviewed, Table 1. In addition, the general operation; the type of data obtained; the designing factors that determine effectiveness and the challenges facing their commercialization will be described.

Table 1: Application of microfluidics for the detection of organisms/pollutants in drinking water, wastewater, continental water and seawater.

Real sample/ matrix	Organism/target pollutant	Microfluidic device/detection technique	Ref
Drinking water/potable	<i>E. Coli</i>	Poly(methyl) siloxane (PDMS) device. Loop-mediated isothermal amplification (LAMP) detection.	[34]
	Bacteria (<i>E. coli</i> , <i>Salmonella</i> , and <i>Pseudomonas</i>) and viruses (MS-2 and Echovirus)	Gold-deposited glass slide. Electrophoretic transport and electrostatic trapping.	[35]
	<i>E. Coli</i>	PDMS chip. Dielectrophoretic focusing and impedance.	[36]
	Lindane	Polycarbonate (PC). Electric Cell-substrate Impedance sensing	[37]
	Copper (Cu ²⁺), zinc (Zn ²⁺), potassium dichromate and 3,5- dichlorophenol	Glass/silicon wafers. Bioluminescent-cell-based sensor.	[38]
Wastewater	Copper (Cu ²⁺)	Glass/PDMS microfluidic device. Fiber optic sensor.	[39]
	Nitrite	Glass/silicon. Colorimetric.	[40]
	Aromatic amines	Cyclic olefin copolymer. Electrophoresis and fluorescence detector.	[41]
	Potassium and nitrate	Not described.	[42]

		Low temperature co-fired ceramic-based potentiometry/ion selective electrodes.	
	Sulfide	Polylactic acid. Sulfide-based electrode/potentiometry.	[43]
	Ammonium	PDMS. Ammonium-selective electrodes/potentiometry.	[44]
Continental water	Phosphorous	Silicon. Yellow vanadomolybdo-phosphoric acid method/absorbance.	[45-47]
	pH	Poly(methylmethacrylate) (PMMA). Photodiode/absorbance.	[48]
	Sulfite and nitrite	PDMS. Fluorescence.	[49]
	Ammonium	PDMS/glass. Fluorescence.	[50]
	Nitrite and nitrate	Urethane acrylate and pre-polymerized UA photoresist. Absorbance.	[51]
	Nitrite and nitrate	Not described. Absorbance.	[52]
	Organophosphate	Glass/PMMA holder. Potentiometry.	[53]

	Hydrogen peroxide	Glass. Chemiluminescence.	[54]
	Mercury (II)	PDMS/PMMA. Chromoionophore film/ absorbance.	[55]
	Mercury (II)	PDMS/PMMA. Fluorescence.	[56]
	Lead (II)	Cyclo olefin copolymer (COC). Voltammetry.	[57]
	Ethinylestradiol	PMMA. Amperometric.	[58]
	Atrazine	Silicon. Chemiluminiscence.	[59]
	Bacteria	PDMS/glass. Fluorescence.	[60]
	Phosphate	PMMA. Absorbance.	[61]
	Phosphate	Paper. Absorbance.	[62]
Seawater	Salinity	PDMS/Glass. Conductivity/voltage.	[63]
	Cadmium	COC. Electrochemical.	[64]
	Nitrite	PMMA. Absorbance.	[65,66]
	Mercury (II)	Glass/PMMA.	[67,68]

		Fluorescence.	
	Nutrients	Polycarbonate. Absorbance.	[69]
	Silicate	PMMA. Absorbance.	[70]
	Phosphate	PMMA Absorbance.	[22,71]
	pH	PMMA. Absorbance.	[23]
	pH	PDMS. Absorbance.	[72]

2.1 Drinking water

One of the biggest concerns which justifies the need of monitoring water quality is the possible presence of bacteria [36,37], parasites [73,74] or other pollutants [37,38,75-84] that could be harmful for humans, through the consumption of water. Since bacteria, parasites and pathogens are presented in very low numbers in potable water, large volumes of water need to be concentrated down and get analyzed by current detection methods. This is a limitation of the existing technology, therefore multiple methods, including force spectroscopy [85], cytometry [86], laser scattering [73], electrochemical [87] and, electrophoresis [17] are been adopted by microfluidic technology to overcome the extremely low number of bacteria or pollutants to be analyzed in the sample. Another approach to improve detection is to exploit the intrinsic electrical properties of bacteria by the combination of two electrical techniques such as dielectrophoresis (DEP) and impedance measurements [88]. This, integrated and combined with microfluidic devices, has the potential of developing accurate, cost-effective and simple-to-use portable platforms. Regarding pre-concentration of large volumes of sample, the use of integrated commercial membranes within PDMS-based devices have demonstrated to capture $\sim 10^{-1}$ μm -scale particles with high efficiency, due to the complementary advantages offered by microfluidics [34]. It is particularly

challenging to accurately quantify microorganisms that are presented in low numbers ($< 100 \text{ CFU mL}^{-1}$). In order to decrease the detection limit and achieve high-throughput analysis, a device that increases the concentration of bacteria by positive dielectrophoretic impedance *E. coli* focusing was proposed achieving a 300 CFU mL^{-1} of detection limit with a sensitivity of 100 CFU mL^{-1} [36], Figure 2A. As an alternative to the use of commercial membranes, electrical forces can be used to pre-concentrate, by exploiting the negative surface charges on bacteria and viruses [35].

Interestingly, mammalian cells have been used as sensors for toxicity measurements of toxicants like lindane [37]. It is known that a major limitation of using mammalian cell-based biosensor for field-testing is the difficulty of maintaining cell viability and sterility outside of a cell culture facility, so devices pending on cells performance will be not practical to scale to commercialization. By adding a self-contained disposable media delivery system to the sensor, cells are kept alive but still the model does not meet market requirements.

Other analytes of interest in drinking water that have been investigated in microfluidic devices are metals, such as copper [38,75,80,84], lead [76], semimetals like arsenic [81], water safety indicators such as nitrite and nitrate [77,82], total concentration of calcium and magnesium [78] chlorine [79] and iodine [83]. For instance, the presence of copper in drinking water usually does not exceed more than few milligrams per liter, although higher concentrations could be detected in waters coming from newly installed copper pipes. For this reason, it is of great importance to be able to monitor effectively copper in pipes. Bioluminescent analyzers that use living organisms as sensors, integrated within microfluidic systems, allow the monitoring of heavy metal ions such as copper and zinc. As a real application example, these devices were used in the analysis of water samples taken from Tønsberg's pipes in Norway. Considering the sensitivity of the system, acute toxicity, it is appropriate as a warning device rather than an actual quantifier of toxicants [38]. Higher sensitivity would be necessary to be able to commercialize these type of drinking water household systems.

Numerous microfluidic-based developments have been made to improve safety in drinking water. The future of accurate, portable microfluidic systems to monitor safety in potable water is in continuous evolution and has not been delivered to society yet.

2.2 Wastewater

Waste and sewage waters are generated by a variety of sources, where the concentration and type of contaminants found in them have high variability thus, the detection methods employed for the analysis should be adaptable as well as comply with regulations and quality standards. Its quality can be affected by several factors including the presence of chemical pollutants and pathogens, which have a real negative impact in human health and ecosystems and may create a real risk for animals and humans existence. As an example, wastewater systems are currently being monitored to determine the levels of SARS-COV-2 virus [89,90], to identify and surveillance the incidence of the virus on the community. For this reason, the routine monitoring of pollutants in wastewater systems, involving simple and inexpensive technologies, is a priority in society. In this sense, microfluidics have proven simultaneous quantification and monitoring of the presence of a wide range of pollutants in wastewaters [91].

For instance, copper is a recurrent metal to be determined in water. In this regard, a hybrid glass/PDMS microfluidic device coupled to an optical sensor was developed for the determination of Cu (II) in industrial wastewater [39]. A specially designed chip minimized reagent and sample consumption and reduced waste generation compared to conventional methods. This technology seems very promising for commercialization and implementation in industrial wastewater systems.

As a step forward to get deployable devices micro-flow-injection analysis (μ FIA) coupled to microfluidics has been using for nitrite determination. The μ FIA was used for nitrite determination, using the Griess-Ilosvay reaction. It is remarkable to mention that the system was placed on-line in a wastewater treatment plant. The optical measurements were performed using a light emitting diode (LED) as emitter and a photodiode as a detector. This system proved to be accurate in two concentration ranges (0-50 and 0-250 mg L⁻¹) with features comparable to those provided by conventional methods [40].

Aromatic amines, which have been demonstrated to be carcinogenic and mutagenic even at very low concentrations, can be released into the environment from industry along with waste. A simple, sensitive and rapid method will be to use electrophoresis within microfluidics. It has a remarkably low detection limit (nm L⁻¹ range), good

repeatability and recovery rates (85-110 %). If a pre-concentration technique is applied to this method, concentrations in the range of pmol L^{-1} would be determined [41].

Microfluidics technology has not only been applied to land-based samples. This technology has also arrived to the space [42]. A low temperature co-fired ceramics, with a continuous flow potentiometric microanalyzer, was developed to simultaneously monitor the presence of potassium and nitrate in samples from the water recycling process in space missions. The microsystem integrates a microfluidic device and two ion-selective electrodes, built with nitrate and potassium polymeric membranes and a screen-printed Ag/AgCl reference electrode. Through the development of this system, integrated and compacted devices for the simultaneous determination of multiple analytes on-field was demonstrated.

Integration and portability are the keys to obtain devices that could be implemented on-field and thus, commercialized. For instance, a sulfide-selective potentiometric sensor integrated in a 3D microfluidic system was tested in wastewater samples, Figure 2B. The device performed with real samples, showing no significant differences when compared to conventional methods [43]. The same year, a transducer coupled to a microfluidic device for the ammonium-selective sensing in the sewers of the Berlin network was published, with a limit of detection of $4 \cdot 10^{-5}$ M and a response time between 10 and 12 s. The key feature of this device was its ability to perform electrochemical measurements combined with passive microfluidics in real-time [44]. The use of passive flow for sampling eliminates the need for external pumps and valves and thus, reduces power consumption, while increments portability and integration. As demonstrated in this section, there is a growing interest in the development of integrated microfluidic devices for the analysis and monitoring of wastewater at the point of need.

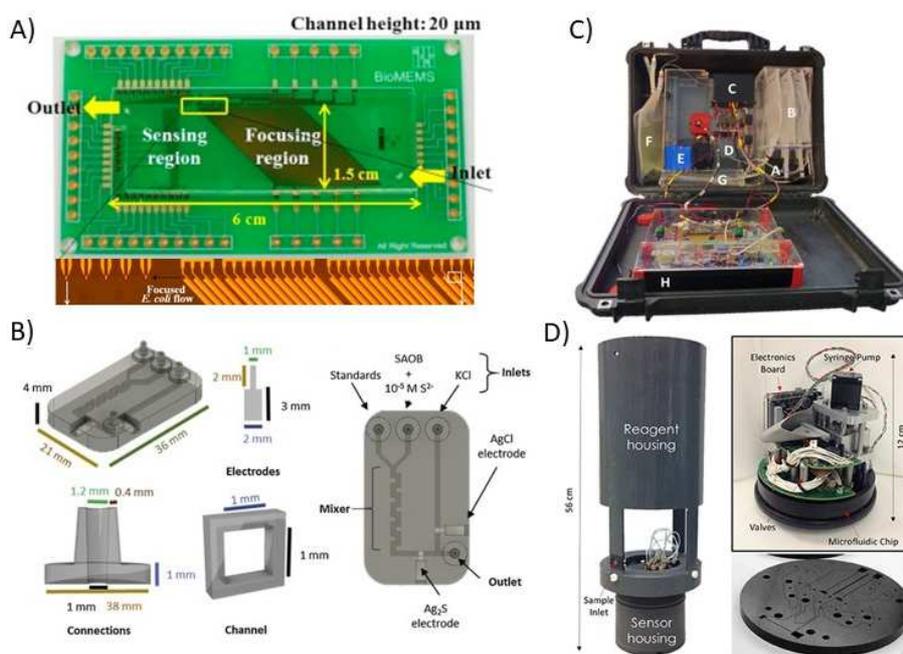


Figure 2: LOC systems developed for different water matrixes. A) Bacteria sensor consisting of a region that utilizes positive dielectrophoresis for *Escherichia coli*-focusing, and an *E. coli*-sensing region that employs dielectrophoretic impedance measurements in drinking water samples [36]. B) Scheme of the fabrication and functioning of the 3D microfluidic device showing locations of the electrodes and dimensions used for the detection of sulphur in waste waters [43]. C) Picture of an autonomous sensing platform for phosphate analysis in continental waters. Inside picture: (A) Inlet system, (B) bags holding sample, high calibration standard, and low calibration standard, (C) detection chamber housing the microfluidic chip, LED (375 nm), and photodiode, (D) poly(methyl methacrylate) (PMMA) fluidic board, (E) battery, (F) reagent Bag, (G) waste bag and (H) electronics [61]. D) Pictures of a LOC phosphate sensor deployed in seawater. (Left) A fully assembled sensor with reagent housing. (Top-right) LOC sensor prior to placement in the watertight sensor housing. (Bottom) One of the PMMA layers of a phosphate LOC (Sensor 1) showing the micromilled microfluidic channels prior device sealing [71].

2.3 Continental water

Continental water bodies are flowing waters, lakes, reservoirs and groundwater. When rain falls to the ground, water keeps moving along the land surfaces to streams or lakes. It evaporates into the atmosphere and soaks into aquifers from which the public drinking water is obtained. Unfortunately, the ground water can be contaminated by chemicals or pollutants and thus also, the deposits of public water [92]. Therefore, the

continuous monitoring of these waters is of great importance to manage and protect water ecosystems. In this context, microfluidic-based devices and sensors are capable of monitoring water quality and so, identifying pollutants in continental waters.

Many developments have been published for the monitoring of nutrients within continental waters. In the following section, we will briefly introduce some of the most inspiring examples. Diamond's group was a pioneer, by publishing a microfluidic device sensor for long term phosphate monitoring, which incorporates fluid sampling, reagent storage, detection and wireless communication into a portable platform. The device was improved over the years, in terms of fluidic handling to reduce dimensions and final cost of production [45-47]. Later on, the same group presented a portable and fully autonomous sensor platform for *in situ* pH measurement of water samples. This sensor has the advantage of having integrated reagents storage, which are stable for up to 8 months with proved reproducibility and good repeatability. It is remarkable the effort that this research group have done for years in the development of portable and autonomous water sensors, devices and systems [61,93], Figure 2C. At the same time, examples of simultaneous determination of sulfite/nitrite in pond and river waters [49], ammonium in rain a river waters [50], nitrite/nitrate in lake [51] and river [52] have appeared. Overall, this sensors comprises valves, pumps, the fluidics and the reagents handling. Some of them are deployed for over three weeks, measuring more than 160000 samples. In this case, despite the high measurement frequency, the fluid consumption of the sensor was remarkably lower than those in previously reported systems [52]. Low fluid consumption is important as this, along with power considerations, determines the length and/or measurement frequency of a sensor deployment.

Regarding analysis of pollutants, organophosphate nerve agents such as paraoxon and methyl parathion were detected in river water samples. The integrated system offered rapid and simultaneous measurement at micromolar levels of both poisons [53]. Hydrogen peroxide, when presents in rainwater, is an efficient oxidizer of sulphur dioxide to produce sulfuric acid, an important compound in acid rain formation. This hydroxen peroxide has been collected from rainwater and snow and analyzed by chemiluminescence [54]. In addition, metals present in continental waters can seriously affect marine fauna and flora therefore, Hg (II) [55] [56] and Pb (II) [57] were analyzed in river water samples using microfluidic technology.

As in potable and drinking water, the control of bacteria and pathogens growths in continental waters is of great importance to avoid intoxications and ensure humans safety in recreational waters. In this regard, immunosensors have been selected as gold standard for rapid quantification of acethinylestradiol [58] and antrazine [59] in river water samples. These devices showed high versatility and suitability for Point of Care analysis, with the possibility of building up array systems. Recently, bacteria have been detected by counting active bacteria stained with fluorescence dyes, 6CFDA- and SYBR Green II-staining. The number of bacteria analyzed with the portable microfluidic system was compared to conventional fluorescence microscopy showing no significant differences. However, smaller cells such as esterase-active cells were not accurately determined [60].

Czugala *et al.* [94] described a wireless paired emitter detector diode device as an optical sensor for water quality monitoring in a lab-on-a-disc device. This technology allows the analysis of a high amount of water samples at the point-of-need without the need of any external energy input. The microfluidic platform was applied for the quantitative pH and qualitative turbidity monitoring of water samples at point-of-need. Fresh river water samples were analyzed using the device, obtaining very good correlation with standard bench-top systems.

It is remarkable to mention that paper microfluidics have emerged as a cheap alternative to polymer-based microfluidics. They also offer less reagent consumption and easier on site measurement. Jayawardane *et al.* [62] evaluated a paper-based device for the determination of reactive phosphate in natural and soil waters based on the formation of phosphomolybdenum blue. The described device is low cost, fast and portable and, in a green chemistry perspective, the device uses less reagent than conventional laboratory devices. A general drawback found in microfluidic paper-based devices is their lack of robustness when long-term deployment is needed. Nevertheless, it is a new technology in continuous development, which will bring smart solutions to deployable water monitoring devices.

2.4 Seawater

The quality of seawater depends in to a great extent on the equilibrium in the concentration of compounds as nitrite, nitrate, ammonium and phosphate, which are

denominated as nutrients, and salinity. An excess in the concentration of nutrients could lead to a detrimental state for the marine fauna and flora. In addition, physico-chemical parameters such as pH, temperature and conductivity among others are of importance to monitor water quality and to prevent deterioration, which may be lethal for marine ecosystems. Microfluidic devices are very interesting when integrated on industrial processes such as desalination plants. On this regards, integrated microfluidic sensors that measure temperature, conductivity, and salinity from harvested water from a pilot-scale desalination plant over a short period have been developed [63]. pH has been measured in LOC by colorimetric assays coupled to a robust optical set-up and short-term deployed in European waters with high accuracy (0.001 pH, $n = 20$) and precision (0.004 pH) [23]. Others, have worked on pH colorimetric assays based on meta-cresol purple as indicator dye, featuring high resolution (0.002 pH units for the 7.500-8.200 range), and linearity (R^2 of 0.9994) but lacking of fully autonomous performance [72]. The work presented by Yücel *et al.* [95] evidences a clear example of integrated deployable microfluidic device that was submerged in the deep ocean and set in seafloors for two days.

During the development of Lab on Chip devices, fluid flow analysis systems, highly integrated and with fast analysis capabilities have become a trend. It is difficult to find examples of integrated sensors that are able to continuously monitor, for long period of time, with high accuracy, low water consumption and strong anti-interference ability [70]. Therefore, microfluidics capable to perform long-term autonomous sampling for seawater environmental monitoring have not been widely reported yet. Nevertheless, several examples of on-site water analyzers for heavy metals, cadmium, determination [64], nitrite [65,66], phosphorous [22,71] and mercury [67,68] were published.

Autonomous systems for the determination of phosphorous in seawater based on the valadomolybdate method have been published [22,71]. We will like to highlight specially the work done by Gran *et al.* where not only the long-term deployment of a phosphate LOC analyzer is demonstrated, but also the close proximity in terms of accuracy and precision to reference standard methodologies [71], Figure 2D.

Despite the huge efforts made in the development of autonomous microfluidic devices for seawater applications, no examples of real implementations have reached the market. Deployable devices should appear in the coming years to reduce the gap

between laboratory experimentation and product commercialization, though device validation in real scenarios.

In particular, it is interesting to mention the use of centrifugal microfluidics for seawater analysis. The simultaneous determination of nitrate, nitrite, ammonium, orthophosphate, and silicate in coastal seawater samples, collected from Chunsu Bay, South Korea, was presented [69]. The device integrated all processes (sample filtering, metering, mixing, reaction, colorimetric detection) and liquid flow was controlled by laser irradiation on ferro-wax based microvalves. This device could be potentially used on site if an autonomous CCD platform similar to [24] would be adapted. Despite of centrifugal microfluidics are gaining attention for biomedical applications, companies fail on the commercialization of these products in the environmental sector due to the elevated cost of both, the disposable device and the platform.

3 Functional Materials Integrated into Microfluidic Devices

Even though microfluidics allows for the fabrication of small devices, the components needed for fluid control (pumps, valves, mixing units) and detection are usually bigger than the device itself, reducing their applicability in real scenarios, thus limiting their commercial value [96]. Here is where functional materials, commonly named as smart materials, arise as suitable alternatives to conventional components for microfluidics, mainly as sensors and actuators.

Functional materials are stimuli responsive materials with an autonomous behavior in response to changes in their local environment, which is essentially dictated by the functional groups present within their polymer chains. These materials can change some of its mechanical properties, such as shape or position, in response to a chemical change [97], magnetic field [98], electricity [99], pressure [100], or light [101] induction and variations in temperature [102] or humidity [103] being able to perform functions, by those external stimuli, without human manipulation, as actuators and fluid controllers. Moreover, if sensing functionalities are incorporated within these materials, they can be used as sensors [104], Table 2. Several groups are working on the integration of functional materials into microfluidic devices for water monitoring [105], and most of them, have described ingenious uses of functional materials which,

under controlled laboratory conditions, exhibit integrability and low-cost compared to conventional ones. Some of these materials include the use of carbon nanotubes for the generation of actuators and for dielectric elastomers to create flexible electrodes [106]. Therefore, these new type of actuators, fluid controllers and sensors, with integrated functional materials, have the potential to improve environmental analysis systems.

Table 2: Functional materials used as actuators, fluid controllers and as sensors in microfluidic devices for water analysis.

Material	Actuator/Fluid driver	Sensor
Poly(<i>N</i> -isopropylacrylamide) (pNIPAAm) hydrogel	Light [94] Temperature [148]	-
pNIPAAm ionogel	Temperature [144-147][152][154]	Colorimetry: Nitrates [27, 173], pH [24]
Poly-ionic liquid tributylhexylphosphonium sulfopropylacrylate (PSPA)	Temperature [137]	-
Spiropyran hydrogel	Light [127]	-
Spiropyran ionogel	Light [161-162]	-
Graphene modified pNIPAAm	-	Electrochemical: pH [142]
Alginate hydrogel	pH [157-158]	-
Agarose hydrogel	-	Fluorescence: Nitrite [169]

Stimuli responsive materials present switchable chemical properties, mechanical strength, tuneable permeability and mouldable surface characteristics, making them very suitable alternatives to conventional fluidic equipment [107]. The functional materials employed in microfluidics can be encompassed in metallic composites [108], hybrid materials [109], magnetic material [110], and polymeric materials [111]. These materials have the ability to change their shape, stiffness, position, natural frequency, damping and/or other mechanical characteristics in response to a chemical, temperature variation, electric field and/or magnetic field [112]. Hydrogels, being one of the first functional materials integrated into microfluidics, are three-dimensional structures of hydrophilic polymeric chains cross-linked into an insoluble, but highly hydrophilic structure swollen in water [96]. The nature of the monomers on the structure, the functional groups and crosslinker's bonding nature define the properties exhibited by the material, being responsible for, for instance, shape-changing behaviour due to volume expansion (and contraction) when a specific stimulus is applied. Hydrogel materials are evolving by changing the solvent used during synthesis from water to ionic liquids (ILs) in order to enhance their mechanical and hygroscopic properties. Ionic liquids are solvents more thermally and electrochemically stable than water, composed by cations (e.g. ammonium, phosphonium, imidazolium, or pyridinium) and anions (e.g. dicyanamide, chloride or acetate), with a melting point below 100 °C and high flexibility [113]. By choosing the appropriate ion pair, the physico-chemical properties of the IL such as viscosity, density, melting point and conductivity can be tuned, in some degree, to suit a particular need. The combination of an IL and a hydrogel component, such as organic [114], inorganic [115], or hybrid organic-inorganic [116] are called ionogels. For instance, when comparing the swelling behaviour and the stability of hydrogels and ionogels, an enhancement of the properties of the material is found as a consequence of the incorporation of the IL in the structure of the gel [117-121]. Moreover, due to their low vapour pressure and their ability to plasticize the gel network, ionogels exhibit high resistance to cracking and drying, which renders them as attractive materials in soft actuators and so, in microfluidic device applications. Several applications have been already presented in the literature regarding ionogels in microfluidics, some of them out of the scope of this review [122,123]. Temperature-responsive materials have been the most widely studied for the creation of *in situ* devices, nevertheless the

need of heaters to induce actuation is an enormous drawback. Therefore, light irradiation, which allows for non-contact operation and possible independent and remote manipulation of multiple fluids, is becoming an alternative to generate actuators in microfluidic devices. Many research groups have studied photoresponsive polymeric materials, mainly functionalized with azobenzene, leukochromophore and spirobenzopyran [124-127] for this end.

The natural evolution of functional materials is leading to the recent incorporation of poly(ionic liquid) (PILs) hydrogels that are polyelectrolytes that feature a combination of IL monomers, connected through a polymeric backbone to form a polymeric architecture [113]. Although most of the researches are focused on linear PILs, several reports are dealing with crosslinked PIL networks [128-133] used as membranes [134], electrolytes [135], sensors [136], and actuators [137-139] in microfluidic devices.

The different functional materials will be introduced and linked to their type of actuation/sensing capabilities. In general, we will try to evidence that, by incorporating different stimuli responsive materials, as actuators or sensors in microfluidic devices, device complexity can be reduced, when used for environmental applications, increasing their potential marketability. We will critically review the integration of functional materials into microfluidic devices, as actuators or fluid controllers and sensors, to eliminate external pumps and valves or to improve sensing capabilities. These materials will be catalogued emphasizing the advantages that they provide, when incorporated in water monitoring systems, which could lead to marketable devices.

3.1 Actuators and fluid controllers in microfluidics

Traditionally, fluidic control in microfluidics use pneumatic and hydraulic valves and pumps that require of additional external equipment, reducing the portability, increasing the price of the final device. Nonetheless, by introducing functional materials as an alternative to conventional fluidic handling equipment, both portability and price reduction are accomplished, favouring commercialization. The intention of this section is to review the different materials used as actuators and fluid controllers but not the actuator mechanism, that has been reviewed elsewhere [106] [140].

As mentioned before, temperature is widely used to generate actuators in microfluidic devices [141-143]. pNIPAAm is one of the most popular temperature-sensitive

multifunctional hydrogel used in microfluidics [144-147]; however, none of these works reveals their applicability for environmental monitoring. pNIPAAm hydrogels, being a dynamic polymer, are controlled by electronic heating elements [148,149], magnetic fields [150,151] or light [152-154], introducing the necessity of external controllers that are not wanted in portable devices. Nevertheless, a drastic change in the volume of a material can be triggered by other stimuli, such as pH. Some authors have developed actuators that respond to changes in pH in a physiological range [155], or even actuators with combined responses [156]. Moreover, pH sensitive hydrogels can also be used for other purposes, for instance, to control the bidirectional transport of reagents in microfluidic devices, Figure 3A [157]. In particular, alginate hydrogels, which are networks of sodium alginate chains typically polymerized with Ca (II) ions, are biocompatible alternatives to be used as thermos-actuators in microfluidic devices for environmental monitoring [158], Figure 3B. Likewise hydrogels, most of the ionogels used in microfluidic devices are based on the polymerization of pNIPAAm, using a variety of ILs [159]. These ionogels have been integrated into lab-on-a-disc as temperature responsive actuators [148,149]. Besides, the swelling properties of ionogels can be employed for liquid flow control in paper devices when the ionogel is used as a passive pump [160].

Another strategy to solve the need for external pumping or mixing [125,126] is the introduction of spiropyran in the pNIPAAm hydrogel [161]. Spiropyran is a photochromic organic compound whose structural change is induced by light and pH. The swelling/shrinking mechanism is reversible and tunable, allowing the control of the flow and mixing in microfluidics, Figure 3C [162]. Additionally, the mechanism can be auto-induced by the copolymerization of spiropyran hydrogels with acrylic acid that introduces the necessary flow of protons needed for the reversion of the structure. It is remarkable to find that, this type of materials were actuated for up to two months in a continuous mode without losing their properties [127]. Spiropyran-based hydrogels have been also implemented in centrifugal microfluidics for controlling fluid motion without the need of external equipment. A white light LED actuated the ionogel valve, making the valve to shrink, allowing the fluid to flow while applying centrifugal forces [162]. In this regard, material robustness and actuation speed of the materials used as actuators is of high importance for the development of microfluidic analysers for long-term deployment, Figure 3D. Moreover, the reversibility of the swelling, the ability

to absorb water [137] and the possibility of controlling flows, make these materials very interesting for the generation of valves and pumps in microfluidic devices for water control.

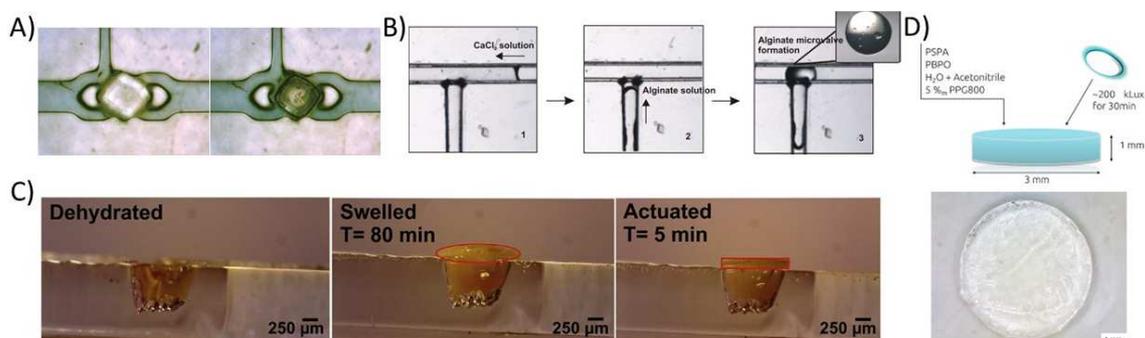


Figure 3: (A) Photograph of the bidirectional valve right actuated by changes in the pH due to the introduction of ethanol, modified from reference [157], B) Photographs showing the generation of an alginate microvalve formation, modified from reference [158], (C) Photograph showing the swelling of a photoswitchable spirobenzopyran valve, modified from reference [162], (D) Photograph showing the structure of a poly-ionic liquid, modified from reference [137].

Therefore, considering the type of materials and publications in this matter, pNIPAAm is an exceptional material easily integrable into water analysis systems to improve valving capabilities and thus, to reduce system dimensions and price. Additionally, the chemical tunability of the properties of this material might provide to water analysis systems with the possibility of multiple actuation processes to control water samples and liquid reagents storage in the same device. As a negative point, reversibility is still a challenge for polymeric pumps and valves being, at this point, less reproducible than external mechanical components. Nevertheless, these materials will be accepted as microfluidic components in commercial microfluidic devices, as long as their price and environmental impact becomes low enough to make the component or the full device disposable.

3.2 Sensors

The IUPAC define a sensor as a device able to detect physical or chemical information and transform it into an analytical useful signal. For that, three basic parts are required: an actuator that controls flows when sensor is working, the sensor itself, that responds

to the change in the environment, and the transducer that recognizes this change and transforms it into an electric signal. Traditionally, electrodes, electric systems, or lasers have been used as transducers [163], increasing the size and final price of the sensors. The emergence of functional materials, was a great advance for miniaturization and for lowering the costs of a sensor, since they can act as both actuators and optical or electrochemical sensor themselves [164].

The ability of hydrogels to change shape by responding to an external stimulus such as pH or temperature has been widely exploited for the fabrication of chemical [165] and optical [166] sensors. Hydrogel sensors consist of two main parts: a hydrogel element and a transducer in charge of converting the swelling signal of the hydrogel into an electrical (change in conductivity or current) or optical (change of fluorescence intensity, diffraction or refractometry) domain [167]; this transducer can be incorporated into the hydrogel in the form of particles. For instance, conductive particles and materials such as graphene can be immobilized in hydrogels to be used as transducers, allowing the use of electrochemical methods [142,168]. In general, these types of microfluidic devices have been developed in the field of biomedicine and biotechnology [140]. Besides their responsive behavior, hydrogels are usually transparent which is a useful feature for sensing colorimetric or fluorimetric reactions. For example, hydrogels of agarose derivatives were used for the fluorescence detection of nitrate in different matrixes, including water, see Figure 4A, [169] obtaining limits of detection in the order of μM . Although, traditional methods are able to detect nM concentrations, this is good example of a sensor that could be integrated in a microfluidic device for water analysis.

The flexibility of ionogels allow their integration into wearable devices [170]. Despite the historical toxicity of some ionic liquids in water [171], the immense majority of ionogel sensors have been developed for biomedical and biotechnological applications due to their biocompatibility, flexibility, and similar properties to biological tissues [172]. In environmental monitoring applications, an ionogel was used by us for the detection of nitrite in water as a proof of concept, Figure 4B [27,173]. The detection of nitrite was carried out using the Griess reaction. The system demonstrates the use of a portable microfluidic device with an ionogel matrix, for water monitoring. Another example of the use of ionogels in the monitoring of water is a Lab-on-a-Disc able to

rotate with a low intensity LED for the simultaneous colorimetric study of the pH and turbidity of water, Figure 4C [24]. On the other hand, PILs, although have not been fully implemented as sensors yet, have been broadly developed as redox modulated supercapacitors and for energy applications [136,138], thus their ionic structure makes them suitable as electrochemical sensors [139].

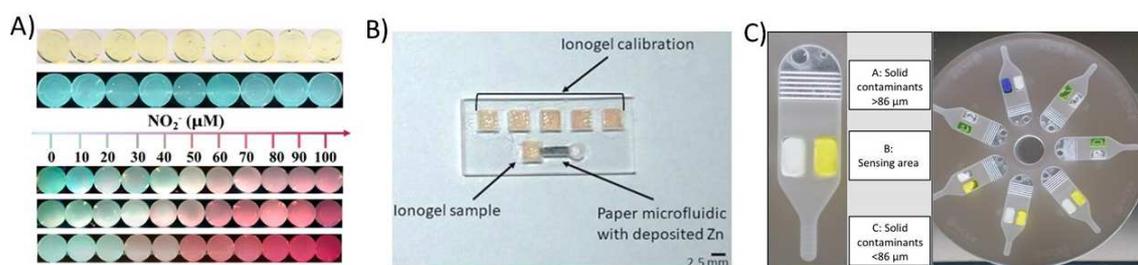


Figure 4: A) Fluorescence detection of nitrate using an agarose based hydrogel, modified from reference [169], B) Photograph of an ionogel-based microfluidic device for the simultaneous detection of nitrate and nitrite, modified from reference [27], C) Photograph of a Lab-on-a-Disc ionogel-based microfluidic device for the simultaneous detection of pH and the turbidity of water samples at point-of-need, modified from reference [24].

Although sensors based on functional materials have been already used for biomedical applications [174], they have just been discretely applied in environmental analysis, despite their potential.

4 Conclusions

The increasing number of publications every year and their high quality demonstrates the great importance that microfluidic devices are acquiring in water monitoring.

Water is principally analyzed by traditional methods such as liquid chromatography and mass spectroscopy spite the huge efforts done to adopt microfluidics in environmental monitoring. Features like miniaturization of the analytical device, *in situ* analysis at the point of need, multiplexing, ease manipulation and control of the device, and low cost during device fabrication will soon bring microfluidics belong the state of the art in water monitoring research.

On the other hand, the use of microfluidic devices comes together with the in-depth study of functional materials and their device implementation to eliminate miniaturization problems of microfluidic components such as valves and sensors, improve the limits of detection by using novel materials and the possibility of creating devices able to analyze more than one analyte. The incorporation of functional materials in microfluidic devices improves automation with novel actuators and sensors, minimizing the need for external bulky components. This will lead to the online, continuous, fast and inexpensive control and monitoring of water sources. Moreover, it will enable a faster and more adequate response to water contamination, even at the point of need.

5. Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 842356, the European Union Seventh Framework Programme (FP7) for Research, Technological Development and Demonstration under grant agreement no. 604241 and the Gobierno Vasco Dpto. Educación for the consolidation of the research groups (IT1271-19). RCC thanks the European Union DNASURF (H2020-MSCA-RISE-778001). University of the Basque Country UPV/EHU with collaborative project COLAB19/05.

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