Chapter 20
Real-Time Monitoring of Water Contaminants for Situation Awareness Using Electromagnetic Field Sensing System

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Abstract Up to 70,000 known and emerging chemical, biological, and radiological contaminants may be present in various water resources. To assure the safety and quality of water and to guarantee the situational awareness of safe water supplies, efficient real-time measurement methods with superior sensitivity are required. Current measurement methods of pollutants are mostly based on off-line monitoring which implies low frequency data sampling, delays between sampling and results, and additional chemical use. In this study, a novel sensing system where the interaction of the electromagnetic field with the tested fluid reveals its composition is presented. In particular, it is suggested that microwave based sensors are a suitable technology to fulfill the requirement for a real-time water pollution monitoring platform. A prototype microwave sensor in the form of printed Cu pattern on FR4 substrate was designed and tested for its response to air, deionized water, 500 ppm phosphate solution, and cooking oil samples. This sensor operates based upon the interaction of the electromagnetic waves and the material under test, which manifests itself as a unique spectra as measured for each sample due to its specific permittivity. By considering how the reflected microwave signal (in a form of S_{11} parameter) varies at discrete frequency intervals, the change in the signal can be linked to the composition of the object under test.

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20.1 Introduction

Surface water reservoirs and aquifers are exposed to contamination by thousands of pollutants from industrial, pharmaceutical, agricultural and natural origins. Known [1] and emerging [2, 3] contaminants that might be present in various water resources pose a real threat to humans and require continuous monitoring for situation awareness.

Wastewater also carries such micropollutants as pharmaceuticals and hormonally active substances [4]. So far, there is little scientific evidence as to the detrimental effects of these compounds on aquatic organisms and the quality of water for drinking [5]. However, as these compounds are considered to be harmful, approaches for the removal of micropollutants from wastewater have been developed either at the source or using new end-of-pipe technology [6]. The chemical industry—including the pharmaceutical industry—is becoming progressively more aware of environmental problems and has increased interest in novel real-time water pollutants monitoring systems.

Water quality assessments are based on the analysis of the physical, chemical and bacteriological parameters and require customized apparatus and trained staff. Physical, chemical, biological and radioactive variables vary widely in all types of water and some high concentrations may be difficult to reduce during the treatment process. In conventional end-of-pipe systems, a large part of the pollutants will always be lost to the environment due to leaking, primarily during rain. In the long term, source separation offers the more sustainable solution to the entire wastewater problem, including organic micropollutants. Urine source separation is an elegant solution to the problems of nutrients and pharmaceuticals alike and losses of untreated pollutants to the environment can be minimized [5]. With continuous industrial developments, depleting natural water resources, and increasing population and its corresponding increased demand on domestic and industrial water consumption, it is getting more and more challenging for the water supply industry to maintain water safety.

Another group of human waste contaminants consists of pesticides, which are usually washed with surface water from agricultural regions [7]. There are also various toxic compounds generated by microorganisms (e.g. microcystins) or multicellular organisms existing in the water. In all developed countries, there are defined legislation and regulatory authorities enforcing maximal residual levels of the various contaminants. Microcystins that result from the blooming of toxigenic cyanobacteria [8] can cause severe poisoning episodes in animals and humans when present in drinking water in sufficiently high concentrations.

Notably, most pharmaceuticals compounds are not routinely monitored in drinking, surface, or wastewater; although a large numbers of compounds were detected when such tests were conducted [6].

Traditional methods of water quality control are lab based and include standard UV–vis measurements, mass spectrometry, ion-sensitive electrodes and amperometric sensors. In particular, liquid chromatography tandem mass spectrometry has become a key technique for environmental analysis, allowing the detection of a wide range of polar and non-volatile compounds [6]. On the other hand, a range of modern real-time monitoring approaches exists, for example fiber-optic sensors, MEMs, lab-on-chip sensors and biosensors.

Most of the reported wastewater UV–vis spectrometric applications are based on visual observation and direct comparison of the UV–vis spectra. For example, the main method for phosphorus detection is using a photo sensor which measures the wavelength of a distinct color (e.g. blue or yellow) that results from a chemical reaction between phosphorus and special reagent [9]. The concentration of the resultant dye indicates the concentration of phosphorus in the sample. Sensors based on colorimetric UV spectral measurements are widely used in commercially available systems [10], but they all suffer from a number of limitations. In particular, sample handling is problematic, and the acquisition of a reference spectra and calibration process are necessary for samples of different origin.

Fiber optic sensors are used in combination with the UV–vis methods of water contaminants detection. Normally an optic fiber is suitably doped to produce luminescence when exposed to an excitation light source. Glass fibers are either doped with a rare earth metal or activated with a transition metal. Polymeric fibers are doped with a dye. The fibers have fast response and decay times and can achieve high efficiency through the design of appropriate delivery optics. Fiber optic systems are particularly suitable for harsh and difficult to reach places. The design and selection of the fiber determines the peak wavelength of the output illumination; options exist to span the UV–Vis–NIR spectrum [11].

Amperometric, potentiometric and conductometric sensing approaches are widely used in the measurement of pollution in water [12]. These sensors change their properties as a result of interaction with the component being measured. The species of interest are either oxidized or reduced at the working electrode causing a transfer of electrons, thus generating a measureable signal. This change can be recorded as a change in the output signal, i.e. output voltage, current, change in conductivity, capacitance or dielectric constant – whatever parameter gives the most pronounced sensor response [13]. Potentiometric detection is attractive since it possesses numerous advantages when considering the development of real-time sensing technologies, as the recording instrumentation is cost-effective and highly portable. For example, a portable amperometric three-electrode immunosensor for screening of polycyclic aromatic hydrocarbons (PAHs) in water was recently reported [12]. In particular, amperometric detection is based on the measurement of current when a potential is applied to the working and reference electrodes of the system.

The presence of microorganisms in water is generally assessed with five indicators, such as total coliform, fecal coliform, fecal streptococcus, enterococcus, and Escherichia coli. To protect public health, microbiological standards have to be met at each individual treatment works and service reservoir. Notably, the presence of various microorganisms in water, including *salmonella*, *campylobacter*, *listeria*, *Bacillus cereus* and *Escherichia coli O157:h7* is a natural and unavoidable occurrence, but the level of these bacteria should be strictly monitored in real time. Infectious doses of these pathogens (as low as ~10 bacterial cells) increase the vulnerability of the elderly, infants, and people with immunological deficiencies or organ transplants [14]. The rise of terrorism has also prompted greater recognition of the importance of *biosecurity* in protecting the environment [15].

Biosensors for the determination of phosphate are normally based on mono- or multi-enzymatic reactions where phosphate acts as an inhibitor or substrate [16]. For example, an amperometric phosphate biosensor, based on a cobalt phthalocyanine screen-printed carbon electrode was recently reported [17] to be successfully applied to the measurement of phosphate in pond water samples and a linear range of 2.5–130 μM with a limit of detection of 2 μM was obtained under optimal conditions, exhibiting a response time of ~13 s. Reportedly, a microelectrode with a tip size ~10 μm fabricated with cobalt wire was designed for in-situ and in vivo environmental analysis of orthophosphate ions (HPO_4^{2-} and $H_2PO_4^{-}$) that evaluates the wastewater phosphorus removal system and for biological applications [18].

Lab-on-chip and electrochemical sensing-based portable monitoring systems appear well suited to complement standard analytical methods for a number of environmental monitoring applications, including water quality monitoring. The concept of a lab-on-chip type system started from the integration of the various chemical operations involved in conventional analytical processes in a laboratory, such as sampling, preparation, mixing, reaction, and separation into a single unified system, requiring only a tiny volume of chemicals and sample and only a fraction of the time needed for the conventional approach. A modern lab-on-chip is a complex system that combines a amperometric/conductimetric sensor, microelectrodes and MEMs arrays, often along with microfluidics facilities.

Thus, within in the last few years, significant advances have been made in technologies to monitor drinking water quality for source water protection, treatment operations, and distribution system management, in the event of accidental (or deliberate) contamination [19]. Generally speaking, however, no single system available today can fully address the needs of the customers, i.e. industries and regulatory authorities, in its ability to determine on-spot, in real time, the composition of water to the desired sensitivity level, bearing in mind the wish for system portability and cost-effectiveness. This could be partially due to the fact that there is no common chemical feature characterizing all water pollutants, except their solubility to a certain level in water [6].

Therefore, novel real-time monitoring techniques are necessary and they must detect the excess of pollutants established by the official water quality regulations [20]. A promising real-time water quality monitoring technique is that of the electromagnetic wave sensor that works within the microwave region.

Microwave sensing technology has been successfully used as a sensing method for various industrial applications [21–23] including water level measurements [24], material moisture content [25, 26], for continuous process monitoring for biogas plants [27] and in the healthcare industry; for example, for non-invasive real-time monitoring of glucose in diabetic patients [26, 28–30].

In one study, a microwave sensor in a form of a cavity resonator for accurate measurements of both organic (sugar, alcohol) and inorganic (NaCl, $KMnO_4$) water solutions concentrations was reported [21]. Notably, the sensitivity of the sensor in determination of NaCl was 0.4 dB/(mg/ml) within 0–1 % concentration range. The sensor was able to detect the concentrations of other water solutions, but its sensitivities are strongly dependent on the type of tested chemical ingredient.

Microwave sensors in the form of cavity resonators or in a shape of printed planar antennas of various configurations operate based upon the interaction of the electromagnetic waves and the material, i.e. fluid sample, being tested. This interaction manifests itself as a frequency change, attenuation or reflection of the electromagnetic signal. By considering how transmitted (S_{21}) and reflected (S_{11}) microwave signals vary at discrete frequency intervals, the change in the signal can be linked to the composition/type of the sample under test.

The microwave planar printed antennas for various sensing applications are increasingly used due to their versatility, flat profile and low weight. Their design can be tailored to suit a particular application, coupled with reliability and cost-efficiency, since they are easily manufactured using common methods for printed circuit board production.

20.2 Experimental Procedure

In this work, a sensor in the form of traditional interdigitated electrodes (IDE) was used to provide maximum interaction with the tested fluid samples. Figure 20.1a shows CAD layout of the manufactured IDE sensor along with its dimensions,

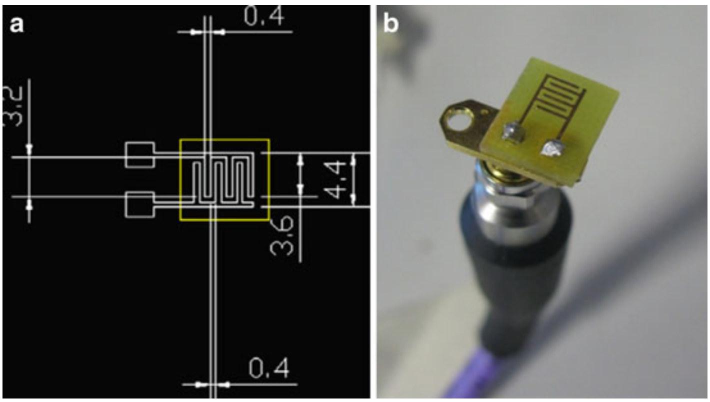

Fig. 20.1 (**a**) CAD layout of Cu IDE pattern; (**b**) Cu IDE on FR4 substrate with SMA connector and N-type cable

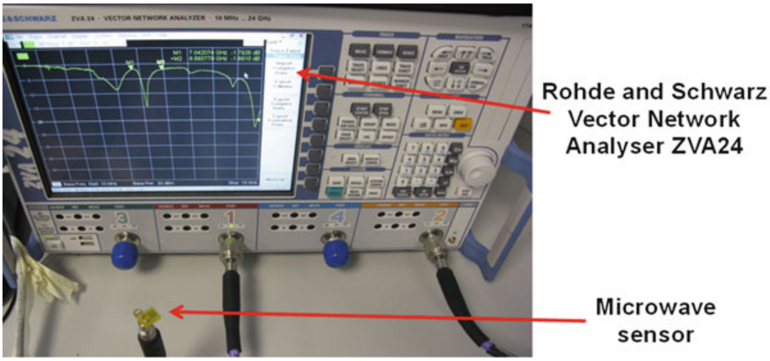

Fig. 20.2 Experimental setup: VNA displays the response of IDE microwave sensor

which are in mm, whereas Fig. 20.1b illustrates the photo of the prototype Cu IDE sensor connected to N-type cable via standard SMA connector. SMA is a very common, popular and easily available connector, which is used to excite a microstrip line or a microstrip antenna. It is mainly 50Ω probe with a central conductor extended to connect the microstrip element. Depending on the size of the antenna or substrate, the connector dimensions may be different [31].

A 1.57 mm thick FR4 substrate (supplied by Mega-UK) covered on one side with 35 μm Cu layer was used. The IDE was subsequently patterned with a Bungarde CNC router. A MOLEX SMA connector was soldered to both arms of IDE antenna to feed the microwave signal. Samples of various fluids, namely deionised water (DIW), 500 ppm phosphate solution (PO_4) and cooking oil (Filippo Berio extra virgin olive oil) were tested (30 μl volume) to verify the applicability of the proposed novel microwave sensor. These were benchmarked against the air spectrum. The experimental setup used to test the IDE response is shown in Fig. 20.2. It comprises a Rohde and Schwarz ZVA24 Vector Network Analyzer (VNA), a microwave sensor and N-type cable to connect the VNA and sensor. The data (60,000 points for each measurement) was captured in the frequency range of up to 15 GHz for the reflected (S_{11}) signal.

20.3 Results and Discussion

Figure 20.3 illustrates the microwave response of IDE in a frequency range up to 15 GHz for air and three different types of fluid, namely deionized water (DIW), 500 ppm phosphate solution (PO_4) and Filippo Berio extra virgin olive oil. From an environmental perspective, the concentration of phosphate in water is crucial due to its role in eutrophication [17]. One can clearly see that the recorded spectra for these samples have unique pattern, with which being accordingly associated the dielectric properties and composition of tested fluid.

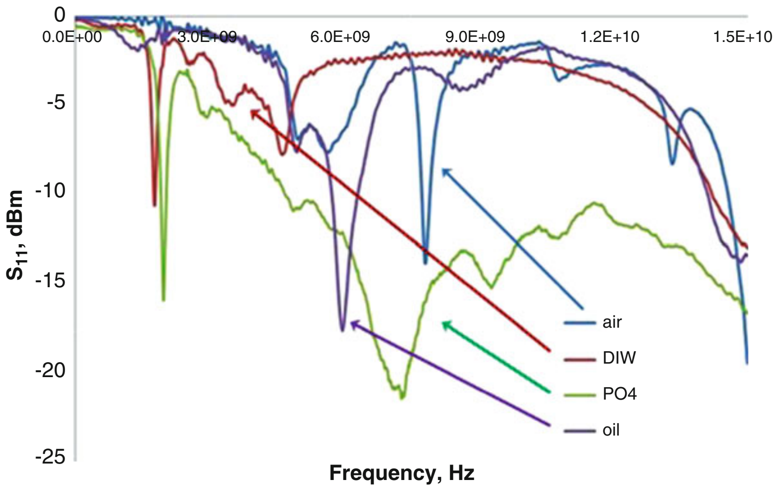

Fig. 20.3 S_{11} spectra for air, deionized water (DIW), 500 ppm phosphate solution (PO_4) and oil (Filippo Berio extra virgin olive oil)

To clarify the principle behind electromagnetic wave sensing suggested in this work for water quality control, it is worth mentioning that microwave sensors in the form of planar IDE sensors operate based upon the fact that an object under test, i.e. fluid, when placed in direct contact with microwave sensor, interacts with the propagating or resonating modes of the electromagnetic field in a unique manner, which can be specifically correlated with the properties of this fluid. Due to this interaction, the dielectric properties of the material can be revealed via frequency change, attenuation, reflection of the signal or its phase shift.

Notably, the sensor dimensions were dictated by a compromise between, on one side, customer requirements for portability and convenience when using the developed water pollution monitoring system, and achieving clearly measurable sensor response with high signal-to-noise ratio to eliminate the need in further signal conditioning and modification.

Importantly, after each sample measurement the sensor response has returned to its original position, namely the air spectrum, which was mostly identical, thus making the sensor reusable for numerous measurements. Small hysteresis could have been caused by a residue cooking oil layer and could be avoided by using an appropriate oil cleaning process between each measurement. Alternatively, new sensor head can be used each time, as the proposed IDE sensor is a cost-efficient solution for real-time monitoring of water pollutants. The observed sensitivity of the developed sensor to various types of fluids suggests that this novel approach can serve as a platform for a cost-effective real-time water contaminants monitoring system.

20.4 Conclusions

There exists a clear need for better on-line monitoring of water systems given that existing laboratory-based methods are too slow to develop operational response and do not provide required level of public health protection. Novel real-time method of water pollutants monitoring is reported. It is based on a microwave sensor system with IDE made from Cu to which a GHz signal is fed via SMA connector and reflected spectra S_{11} is analyzed. Microwave signal experienced a change depending on a type of fluid brought in contact with the sensor. From the database of previously measured test samples, one can determine in real-time what type of water pollutant is present. Other IDE patterns and materials are being explored to achieve the highest sensitivity and selectivity of the sensor response. Moreover, a combination of different sensors into a single system could be an option when a complex mixture of different water pollutants needs to be precisely determined.

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