CHAPTER 2

SENSOR DESIGN

The use of sensors and detectors to continuously detect important chemical properties has significant analytical advantages. By providing a fast return of the analytical information in a timely, safe and cost effective fashion, such devices offer direct and reliable monitoring of explosive compounds. The real-time electrochemical sensor for explosive monitoring capability has been accomplished through on-line or submersible operations.

2.1 Design Criteria

In general, a useful electrochemical sensor must obey a number of experimental design criteria, many of which are linked to its potential benefits. Among the most important are [6]:

(a) For amperometric and voltammetric sensors, the species to be determined is electroactive within the sensor's potential range and whether there is the addition of an inert supporting electrolyte to carry the current perturbs the equilibria in solution.

(b) For potentiometric sensors, there is an adequate electrode material, free from interferences.

(c) The concentration of electroactive species can be determined with sufficient accuracy and precision.

(d) The measurements are sufficiently reliable and repeatable.

(e) The response time of the sensor is sufficiently fast.

(f) The drift or diminution of sensor response with time due to electrode degradation or surface fouling is sufficiently small.

(g) Calibration is simple and easy to perform, or not necessary.

(h) The detection limit is sufficiently low for the purpose envisaged.

A number of critical design criteria that should be considered when designing and developing robust electrochemical sensors for environmental monitoring is listed in Table 2.1 [8]. These are especially true for the development of submersible sensors where microfabrication, portability, analytical response, sensitivity, selectivity, biofouling, reversibility and power consumption issues are of major concern.

2.2 Remote Carbon Fiber Based Electrochemical Sensor

2.2.1 Sensor Design

A schematic diagram of the typical remote *in-situ* carbon fiber based electrochemical sensor is shown in Figure 2.1. The submersible probe consists of a three-electrode assembly, in a 25 mm i.d. PVC housing tube, connected to a 50 ft (24 m) long shielded cable, via a three-pin environmentally sealed rubber connector. Two female coupling connectors, fixed with epoxy in the PVC tube, served for mounting the microcylinder working electrode and the silver-silver chloride electrode reference electrode. These electrodes were sealed into Teflon male fittings, hence allowing their easy and fast replacement. The platinum wire counter electrode was fixed permanently into the housing. Contact to the working and reference electrodes was made via brass screws and spring assemblies, contained inside 7-mm o.d. copper tubes.

Table 2.1 Criteria for the design and development of electrochemical sensors for environmental monitoring [13].

Macro vs. miniaturized fabrication design
Overall cost, simplicity/complexity of design
Robustness, reliability
Sensitivity and selectivity
Reversibility and stability
Speed
Artifact minimization
Speciation capabilities
Automation, data acquisition
Single vs. multicompound analysis capabilities
Low power consumption

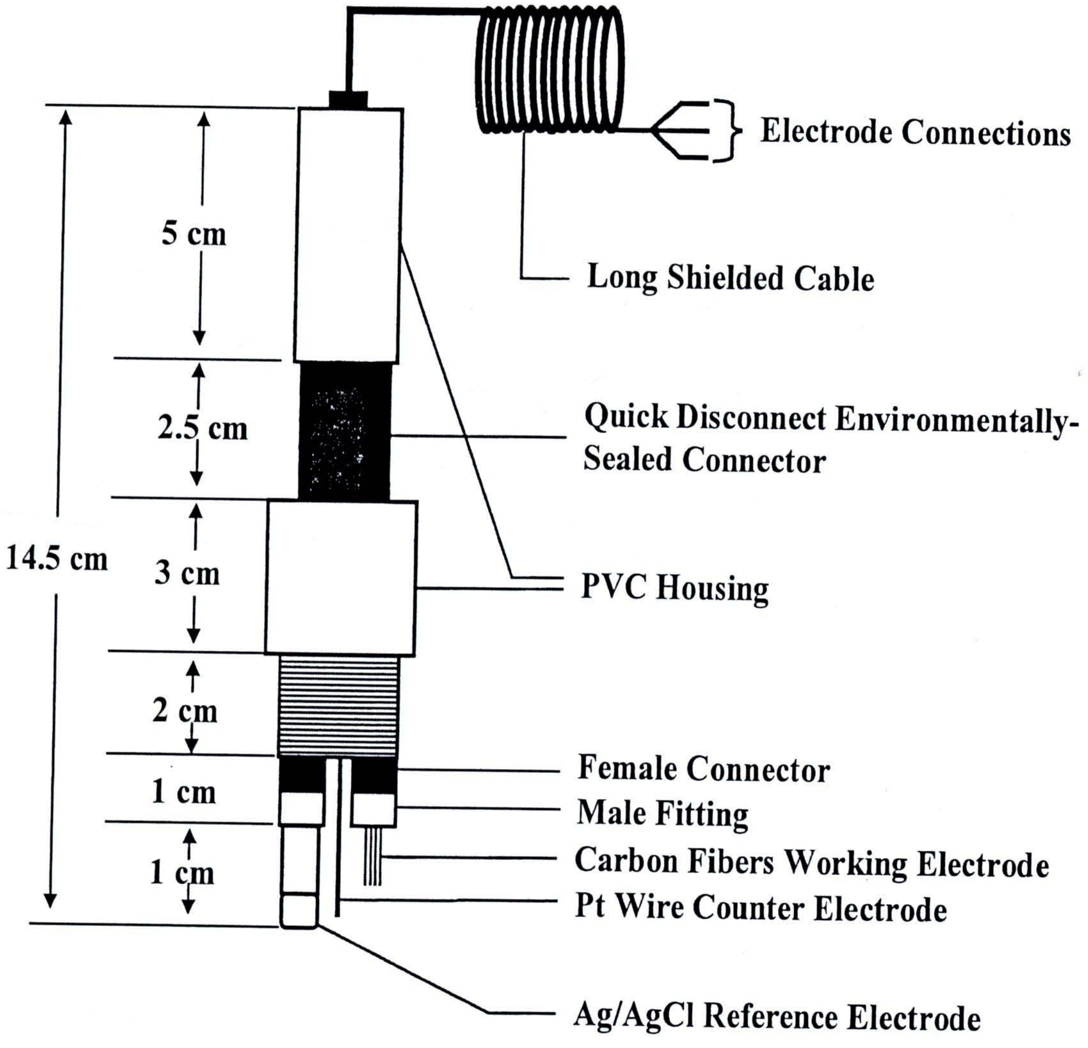

Figure 2.1 Schematic diagram of the remote *in-situ* carbon-fiber based probe.

The latter were placed within the female contacts. The other end of these wires was connected to the male environmentally sealed connector. A similar contact was made to the platinum counter electrode. The male connector was coupled to the receptacle one, which was attached to the shielded cable. Such an arrangement allows rapid disconnection of the electrode housing from the cable. The female connector was also sealed in a PVC tube that provides additional rigidity.

2.2.2 Reference Electrode

The function of the reference electrode is to provide a reference point for working electrode potentials. The reference electrode should, therefore, possess a constant potential value and be chemically stable against solution composition. The commonly employed reference electrode is saturated calomel electrode (SCE) or silver/silver chloride (Ag/AgCl) electrode which has a standard potential of 0.242 or 0.222 V, respectively. In three electrodes system, there is essentially no current drawn through the reference electrode. For the remote carbon fiber based electrochemical sensor, a Ag/AgCl reference electrode (BAS Co.) was used as a reference electrode for all experiments.

2.2.3 Counter/auxiliary Electrode

The function of counter or auxiliary electrode is to complete the electrical circuit where current is allowed to flow between the working and the auxiliary electrodes. The placement of the electrode, with respect to the working electrode, is important as the product of reactions at the electrode may reach the working electrode and interfere. The materials for the counter electrode should be chemically inert. Platinum and carbon are the most commonly employed as the auxiliary electrode. Large surface area, about 50 times larger than the working electrode, is preferable. In the remote carbon fiber based electrochemical sensor, platinum wire was used as the counter electrode for all measurements.

2.2.4 Working Electrode

The carbon fibers microelectrode was used as the working electrode material in the design of remote electrochemical sensor. Due to the number of inherent advantages of carbon fiber microelectrodes of very small dimensions, the use of the microelectrode has become widespread in electrochemical sensors. The microelectrode possesses the advantage of mass transport of analyte to the electrode surface due to non-linear diffusion. This allows the deposition step to be accomplished without the need for stirring the solution, therefore, random errors often associates with the preconcentration step can be avoided.

According to the fact that the surfaces of carbon fibers are very rich in oxygen containing functional groups such as predominantly carbonyl, carboxyl, hydroxyl and ester groups, these functional groups may play important roles in electrochemical reactions. Carbon fibers electrodes have a wider potential window than metal-based electrodes especially in the anodic range. Carbon fibers (6-20 μm diameter) are produced by the high temperature pyrolysis of polymeric materials and they exhibit interesting surface phenomena that can influence significantly the reversibility of redox reactions and the resulting voltammetric response. Three types of carbon fiber electrode have been mainly used: the exposed single fiber with cylindrical geometry; signal fiber or arrays of fibers, embedded in an insulating material with disk geometry; and brushes, or arrays of exposed fibers.

For fabrication of the carbon fiber micro-working electrodes, carbon fibers (8 □m diameter, ALFA AESAR Inc., #1045A) were firstly immersed overnight in 50% ethanol solution, rinsed with distilled water and dried prior to their sealing. Then, a bundle of them (~15 carbon fibers) were placed into a 100 μL standard micropipette tip to a desired distance (usually ~1 cm). The carbon fibers were sealed at the head part of the tip completely with the nail coat insulator and after obtaining the proper part by cutting the tip, it was fixed into a male Teflon fitting. Electrical contact between the carbon fibers and a copper wire was made by back-filling the pipette with the carbon paste and inserting a copper wire (1 mm diameter). Finally, epoxy resin was placed over the carbon paste.

2.3 NPRU Sensor Design

The Nakhon Pathom Rajabhat University (NPRU) sensor consists of three main parts: the electrode unit, the analyzer board and a PC 104 computer. The picture and schematic diagram of the electrode unit is shown in Figure 2.2. The electrode unit has three electrodes: carbon fiber (8 μm diameter, ALFA AESAR Inc., #1045A) working electrode, silver wire reference electrode and platinum wire counter electrode.

To fabricate the electrode unit, cylindrical Plexiglass was used as electrode housing. In the three Teflon male fittings (3 mm diameter) with the screw, the three electrodes were carefully sealed by the epoxy to leave ca. 0.5 cm out and were connected to the copper wires through the graphite powder. The copper wires are long enough for connection with the electrochemical analyzer. The Plexiglass cylinder with the diameter of 3.0 cm and height of 1.5 cm was used to fix the three electrodes. The three electrodes were screwed and fixed in the three holes on the cylinder to leave the three electrodes out for measurement. The distance between every two electrodes was 1 cm. This electrochemical detection system was connected with the interface that can be fixed on the vehicle. In order to detect practical samples such as the sea water, sometimes the three electrodes were protected using plastic tubes with several holes to permit the flow of the sample solution.

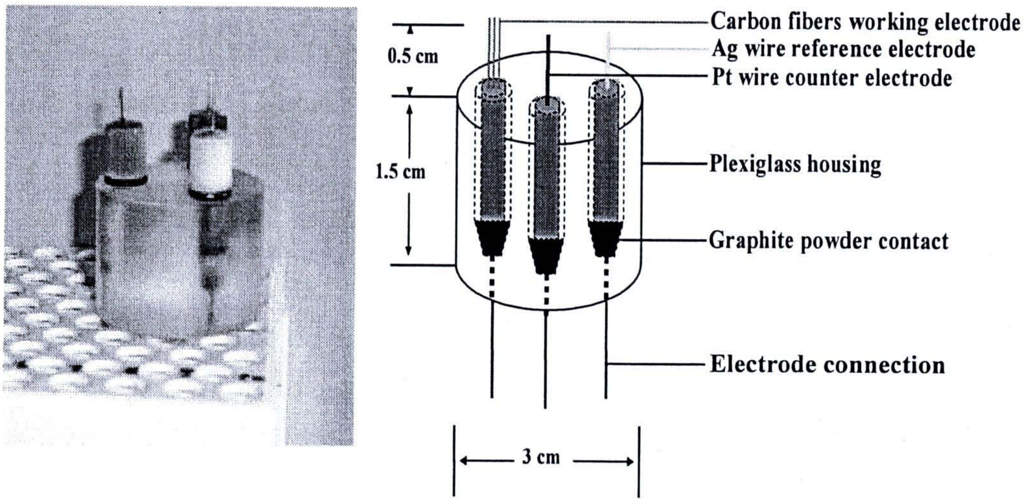

Figure 2.2 The picture and schematic diagram of the *in-situ* carbon-fiber based submersible probe.

The analyzer (also called, potentiostat) performs a function of square-wave voltammetric measurement and is attached to a PC 104 computer via serial connection. Software necessary to control the analyzer board is loaded onto a PC 104 computer which has a Windows operating system. Essentially, voltage is applied between the working and reference electrodes and current is measured between the working and counter electrodes.

2.4 Bismuth Film Electrodes

Over the last two decades, since the invention of polarography by Heyrovsky, mercury has been established as the electrode material of choice for electroanalysis in the negative potential regime, especially for anodic and adsorptive stripping analysis. Starting from the dropping mercury electrode (DME), the hanging mercury drop electrode (HMDE) and later on more robust mercury film electrodes (MFEs), have been used successfully in a lot of applications involving reduction of organic and inorganic electroactive compounds. However, there is a continuous effort to discontinue the use of mercury because of concerns associated with its disposal, leading to potential risks of poisoning and toxicity [10].

As a result, new electrode materials capable of replacing mercury are being continuously searched. In 2000, Wang et al. proposed Bismuth film electrode (BiFE) as an alternate to MFEs. BiFE are prepared by plating a thin bismuth film on a suitable substrate material. Although the most significant advantage of BiFE is their negligible toxicity the analytical properties depicted from voltammetric analysis are roughly comparable to those of MFEs. This phenomenon is attributed to the property of bismuth to form "fused alloys" with heavy metals, which are analogous to the amalgams that mercury forms.

Since the introduction of BiFE, the electroanalytical community has been overwhelmed and there is a concerted effort by several groups to explore the possibility of using bismuth instead of mercury for electroanalysis. Although most of the research has been directed towards understanding the properties of BiFE, some applications in environmental, clinical and food analysis have also started to appear.

2.4.1 Preparation of Bismuth Film Electrode

BiFE primarily uses the same substrates as mercury. One of the widely used substrate is carbon electrode, and different forms of carbon modified with BFE have been reported; glassy carbon, carbon paste wax-impregnated graphite, pencil-lead and screen-printed carbon ink. Although glassy carbon generates a low background current, it is a more expensive material than commercially available pencil-lead and carbon-paste electrodes, which preparation and surface re-generation is easier. Screen-printed electrodes on the other hand can form the basis for disposable, mass-produced sensors. For microelectrode applications, the common substrates that have been used are single carbon fibers, gold and platinum wires. BiFEs based on such microlectrodes are operational in low-conductivity media, give rise to small capacitive currents, allow efficient mass transfer without forced convection and could be applied to small-sample volumes.

For satisfactory performance of the BiFE, it is very important to have a good coating of bismuth on the substrate. There are three general methods of depositing bismuth on the substrate surface; preplating/ex-situ plating, in situ plating and bulk modification of the electrode.

Preplating or ex situ plating, involves prior deposition of a bismuth-film on the electrode surface before transferring the electrode to the sample solution for analysis. An acidic medium is usually recommended for this method to avoid hydrolyzation of Bi(III) ions at higher pH. Since this method requires preplating, a high concentration of the Bi(III) ions in the range of 5-200 mg/L is required. Deposition is performed at a negative potential region in the range -0.5 to -1.2 V with a deposition time of 1-8 min under conditions of forced convection (electrode rotation or stirring).

For in situ plating, a relatively low concentration of Bi(III) ions, typically 400-1000 □g/L are added directly into the sample solution and the bismuth film is co-deposited on the electrode surface along with analytes of interest. To avoid saturation of the bismuth film by analytes under analysis, as a general rule, concentration of Bi(III) must be at least 10 fold in excess of the analyte concentration.

Although in situ plating simplifies and shortens the experimental procedure (as an extra preplating step is avoided), it is essentially only useful in fairly acidic pH region since Bi(III) ions are very susceptible to hydrolyze in neutral and alkaline media according to the reaction [11]:

$$Bi^{3+} + 3H_2O \longrightarrow Bi(OH)_3 + 3H^+ \qquad [2.1]$$

However, quite interestingly it has been shown that operation in highly alkaline media is possible under the postulation that Bi(III) does not hydrolyze but forms stable complexes with OH^- ions which are soluble in aqueous media and therefore are electrochemically reduced [11].

$$Bi^{3+} + OH^- \longrightarrow Bi(OH)^{2+} \qquad [2.2]$$

It is worth noting here that unlike Bi(III), Hg(II) ions hydrolyze under such highly alkaline conditions, and therefore are unoperative.

Bulk modification of an electrode involves introducing a bismuth precursor (i.e. a compound of Bi(III), such as Bi_2O_3) into a carbon paste electrode and applying a potential of around -1.0 V. This forms metallic bismuth deposited on the surface of the electrode upon reduction according to the reaction [12]:

$$Bi_2O_{3(S)} + 3H_2O + 6e^- \longrightarrow 2Bi_{(s)} + 6OH^- \qquad [2.3]$$

These bulk electrodes are easy to prepare and simplify the experimental procedure by providing a means of generating a bismuth film in situ without using Bi(III) salts. However, they suffer from low linearity and shifts in the stripping peak potentials).

Scanning electron microscopy (SEM) was used to study the morphology of the bismuth coating and it was shown to be profoundly affected by the substrate material. On glassy carbon, the bismuth film consists of a porous three-dimensional structure, while on carbon-fiber microelectrodes, a more uniform structure was observed. Furthermore, the potential and concentration of the plating solution controls the thickness of the bismuth film that affects peak height and shape in anodic stripping analysis, depending on the target metal ions. BiFEs are expected to be mechanically more stable than MFEs, since the bismuth film forms a solid deposit, whereas the mercury film consists mainly of liquid mercury droplets on the surface of the electrode.

Stripping analysis often requires a series of measurements, and for this application the surface of the electrode must be reactivated by polarization at a potential that facilitates oxidation (anodic stripping) or reduction (adsorptive stripping) of any species. As far as preplated BiFE is concerned, in anodic stripping voltammetry, a "cleaning" potential is chosen which must lie between the oxidation potential of bismuth and metal ions under analysis. Such a potential is applied for a short time of 10-30 s in a stirred solution. In adsorptive stripping voltammetry, the "cleaning" potential chosen is more negative than the reduction potential of the adsorbed species and oxidation potential of bismuth. On the other hand, the "cleaning" potential in in-situ plated BiFEs is rather less precautious since the bismuth film is stripped off electrochemically after each measurement cycle at a potential more positive than the oxidation potential of bismuth and a new bismuth film is re-plated during the next analysis cycle.

It is worth mentioning two related types of electrodes, the so-called bismuth-bulk electrode (BBE) and mixed silver-bismuth alloy electrode. The BBE essentially consists of a polycrystalline pure metallic bismuth rod and its properties and active surface are similar to those of a BiFE. Such an electrode requires no bismuth-plating step and its surface can be easily regenerated by mechanical polishing. Although mixed silver-bismuth alloy electrode has been reported for use in stripping analysis with satisfactory results, there is lack of evidence and discussion towards its analytical utility and advantages.

2.4.2 Performance of Bismuth Film Electrode

2.4.2.1 Potential Window

The accessible potential range of BiFEs is lower than that of MFEs. While there is no significant difference in cathodic limit, BiFEs in comparison to MFEs suffer from limited anodic potential window owing to the easily oxidizable nature of bismuth. Furthermore, the useful potential window is strongly affected by the pH of the solution. Electrolytes with more alkaline pH allow more negative cathodic limit while more positive anodic limit is achieved in more acidic solutions. A narrow anodic potential range limits the utility of BiFEs in not only the anodic stripping analysis (e.g., Cu, Sn and Sb), but adsorptive stripping analysis as well of metal ions with more positive, or similar, oxidation or accumulation potentials than that of bismuth, respectively.

2.4.2.2 Stripping Modes

The strength of BiFEs is mostly pronounced in applications of trace analysis when coupled to electrochemical stripping methods, which rely on preconcentration of the analytical species on the working electrode prior to a stripping measurement. Stripping methods include stripping voltammetry (linear sweep, differential pulse and square wave) and stripping potentiometry (constant current of chemical as oxidants). In the former, the different techniques are distinguished depending on the nature of the preconcentration process (adsorptive or electrolytic), direction and mode of the voltammetric scan. While most early studies on BiFE have been devoted to ASV measurements, recent activity focused on adsorptive- and potentiometric stripping experiments. In most cases the methodology of detection is adopted from similar procedures on MFEs.

2.4.2.3 Applications of Bismuth Film Electrode

Although most of the earlier work on BiFEs were concerned with insights into their behavior and properties, applications to environmental, clinical and food analysis have started to appear quite recently and are still rather limited. So far the metal ions detected by anodic stripping analysis include Cd, Pb, Zn, Tl, In, and Cu. Within this library, Cd and Pb are probably the most studied metal ions and at trace levels, involving determination in a variety of environmental samples (e.g., hair and tap water, drinking water, and soils), biological fluids (e.g., urine) and food products. Using adsorptive stripping analysis, Ni and Co have been quantified in soils, river water after complexation with dimethylglyoxime, and Cr in tap water, soils, tobacco and certified steel sample (containing 0.7% w/w of Cr) after complexation with cupferron. It is interesting to note Cr determination in certified steel sample showed no interference from co-existing metals (especially from Fe existing in a large excess). There are reports of amperometric and voltammetric determinations of organic compounds on BiFE including 2-nitrophenol and bromofenoxim. BiFE have been further exploited for some novel ideas, for example, using bismuth peak as an internal "built-in" standard for normalization purposes, the use of electrically heated BiFE and combining with ultrasonic accumulation.

2.4.2.4 Interferences on Bismuth Film Electrodes

Interference studies are an important aspect of any analytical technique. For electroanalysis with BiFE, interferences involve adsorption of surface-active compounds, formation of intermetallic compounds, poor resolution between adjacent peaks and mechanical degradation of the bismuth film. Out of these, interference caused by different surface-active compounds is the most important, and is due to fouling of the electrode surface, lowering sensitivity and erratic behavior of the electrode. In stripping analysis, BiFE are as susceptible as MFEs to the presence of surface-active compounds. An elegant solution to this problem that was explored in this thesis involved covering the surface of the bismuth film with a permselective Nafion membrane. Since Nafion is negatively charged, it rejects the surface-active compounds which are negative charged. Besides avoiding interference, Nafion polymeric film on BiFE imparts mechanical resistance to the electrode and enhances the stripping peaks, leading to an increase in sensitivity.

BiFEs have shown some unique advantages with respect to overlapping peaks since they offer a better separation between the Cd and Pb peaks than MFEs. In cathodic voltammetnc measurements, the reduction of dissolved oxygen had been a common interference and thus deoxygenation of the solution by purging with nitrogen or helium was necessary. The advantage of using BiFEs is that it is less sensitive to the presence of oxygen than MFEs, and therefore the time-consuming deoxygenation step becomes insignificant.