CHAPTER 3

SENSOR OPTIMIZATION AND PERFORMANCE CHARACTERISTICS

3.1 Sensor Optimization

3.1.1 Electrode Materials Optimization

The selection of materials for the working electrode is critical to obtain the reliable monitoring of environmental pollutants. Therefore, various electrode materials were examined and compared for their voltammetric signal, background current and overall signal-to-background characteristics. These materials included gold, carbon paste, screen-printed carbon, a Goodfellow carbon fiber, glassy-carbon and a Alfa Aesar^{TM} carbon fiber. The Alfa Aesar^{TM} carbon fiber offered the most attractive performance in terms of signal-to-noise characteristics and was selected for all subsequent work.

3.1.2 Voltammetric Waveform Optimization

Various voltammetric waveforms can be used to produce the current-potential voltammetric profiles. These differ mainly in the excitation waveform and, hence, yield different signal-to-noise characteristics. The responses of the carbon fiber based sensor for heavy metals using linear sweep voltammetry, differential pulse voltammetry and square-wave voltammetry were compared. The square-wave voltammetric profiles yielded the most favorable performance characteristics with detection limits down to 50 ppb. Square-wave scanning rate also can be performed very rapidly (over a 60-second period), thus allowing 60 measurement per hour. No improvements were observed when the square-scan was preceded by a delay time indicating no accumulation of metals onto the carbon fibers working electrode. Most favorable conditions were observed using a square-wave amplitude of 25 mV, a frequency of 15 Hz and a step potential of 4 mV.

Further improvements were obtained using the baseline-subtracted square-wave operation. This effective computer-controlled background-subtraction protocol was developed to correct for high baseline contributions surrounding the metal reduction signal, and allows convenient quantitation of ppb concentration levels. For example, Figure 3.1(A) and (B) display the square-wave voltammetric for a 500 ppb metal solution. In Figure 3.1(A), the square-wave voltammogram for metal "a" and the background "b" signal without metal is recorded in the conventional mode, and in Figure 3.1(B), it is in the subtractive mode. Such large baseline contribution obscures the signal and prevents convenient quantitation of parts per billion (ppb) concentrations of metal. In contrast, the subtractive mode effectively compensates the background signal and leads to a well-defined response signal, with three reduction peaks of three metals.

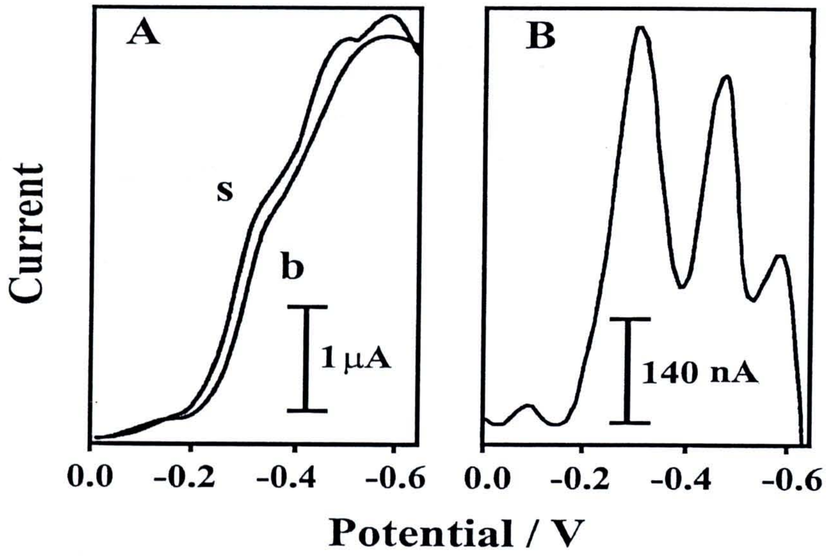

Figure 3.1 Response of the remote *in-situ* carbon-fiber probe: (A) Square-wave voltammograms for the three metals solution of 0.5 ppm each (s) along with the corresponding background (b). (B) Background-corrected voltammogram.

Dramatic improvements, associated with the baseline correction approach, are illustrated also in Figure 3.2 for analogous remote measurements of 0.25 ppm metal. Once again, the effective compensation of the rising background allows convenient monitoring of low parts per billion of metal levels (curves b vs. c). An extremely low detection limit of around 50 ppb can, thus, be estimated.

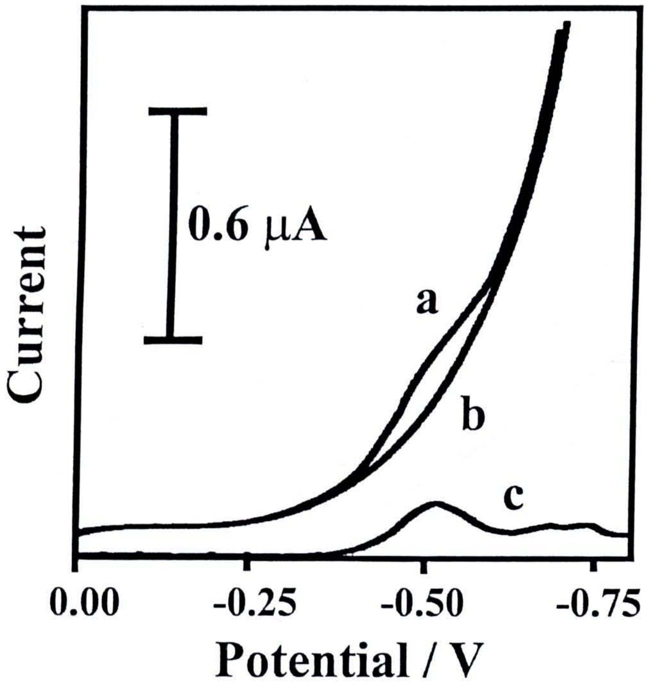

Figure 3.2 Response of the remote *in-situ* carbon-fiber probe to the solution of 0.25 ppm metal solution (a) along with the corresponding background (b) and the background-corrected voltammogram (c)

3.2 Performance Characteristics and Detection Limits

Figures 3.3 and 3.4 depict voltammograms generated with varying concentrations of some heavy metals in laboratory water, respectively. The maximum signal for both metals is directly superimposed onto the oxygen background peak. These results demonstrate small changes in current response relative to large change in metals concentration and results in significantly higher detection limits for these metals.

To improve detection limits and specificity for the metals, one option would be to remove oxygen through purging with an inert gas (e.g. nitrogen or helium) or with the addition of a reducing agent (e.g., sodium dithionite) to the test solution. Figure 3.5 shows the drastic decrease in the oxygen background signal in the voltammogram by simple purging the sample with nitrogen. Based on these results, we anticipate detection limits for the metals on bismuth film electrodes to approach those of the mercury film electrodes.

The analytical utility of the submersible probe is based on the linear dependence between the peak current and the metal concentration. Such dependence was examined for solutions of increasing concentrations over the 100 to 1,000 ppb range (Figure 3.6). Despite these extremely low concentrations, the voltammetric sensor offers convenient detection, particularly when used in the subtractive mode. The peaks are proportional to the metal concentration. The resulting calibration plots (also shown on the right) are linear with a correlation coefficient of 0.979.

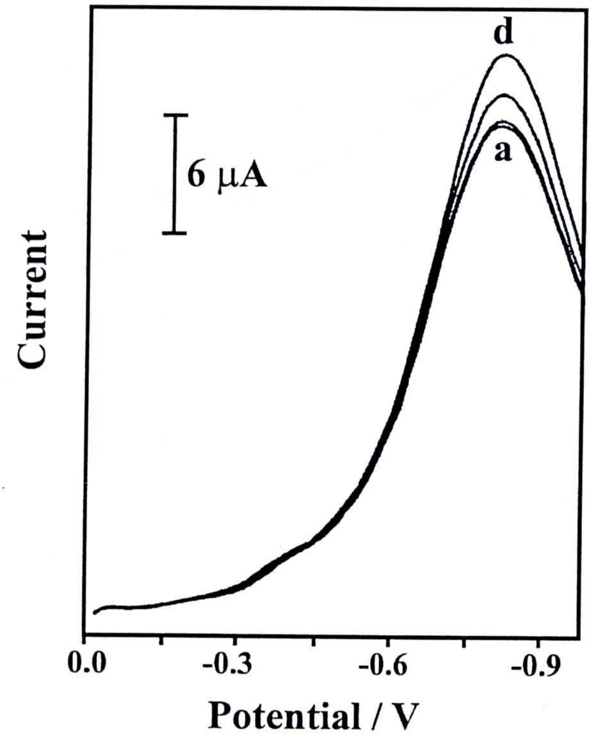

Figure 3.3 Voltammetric response of the remote carbon-fiber submersible probe for 5, 10 and 15 ppm (b-d) metal solution along with corresponding background (a).

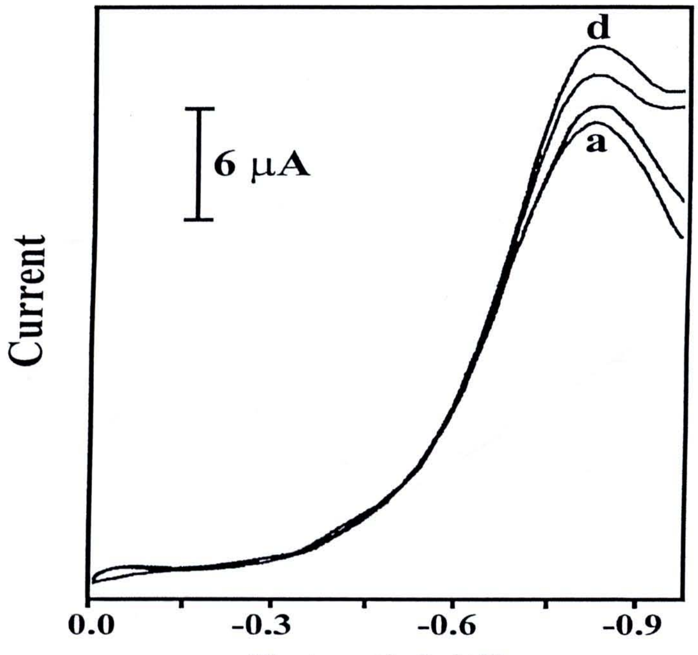

Figure 3.4 Voltammetric response of the remote carbon-fiber submersible probe for 5, 25 and 50 ppm (b-d) metal solution with corresponding background (a).

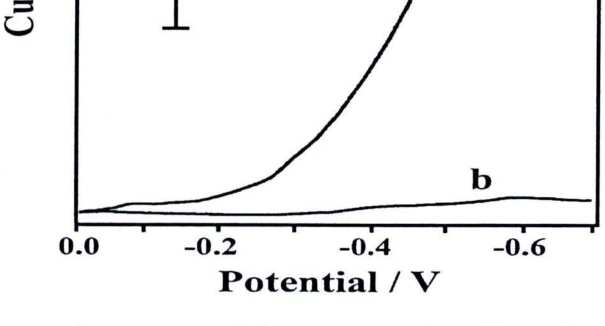

Figure 3.5 Voltammetric response of the remote carbon-fiber submersible probe comparing oxygenated (a) and deoxygenated (b).

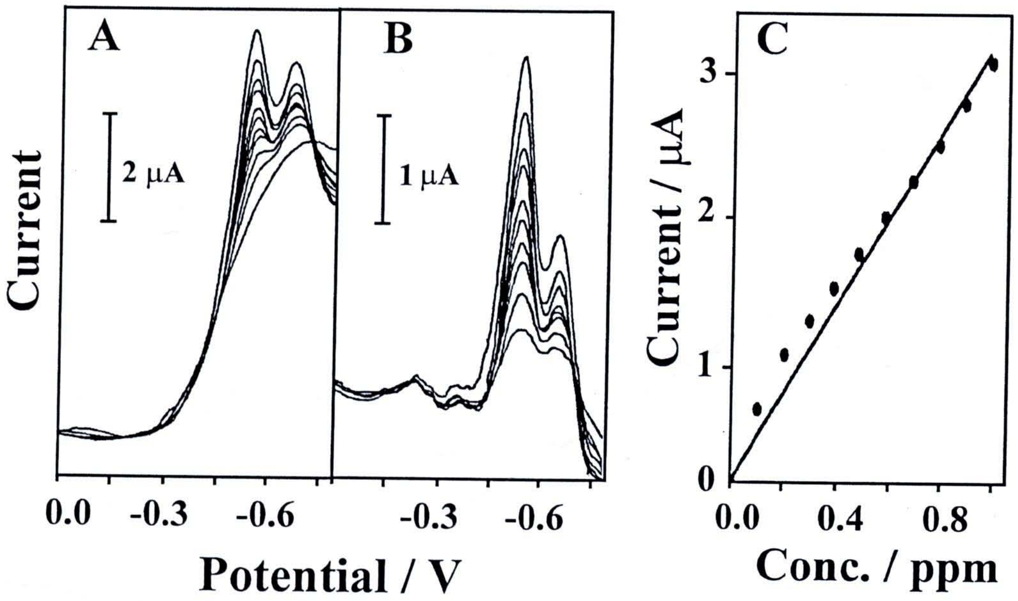

Figure 3.6 Calibration plot (C) obtained with the remote carbon-fiber submersible probe for the increasing levels of 0.1-1.0 ppm metal solution recording with the conventional (A) and subtractive (B) voltammetric mode.

3.3 Stability and Carry Over

The stability of the response has an important bearing on the practical utility of the probe. The carbon-fiber transducer behaved normally over prolonged operations with no apparent surface passivation. The stability was evaluated using a series of 60 repetitive measurements of 2 ppm metal solution over a prolonged (4 hour) period. As indicated from Figure 3.7, such series yielded a highly stable response (for both conventional and subtracted operations, left and right, respectively), with a relative standard deviation of 1.04%. No apparent loss in sensitivity was observed for analogous measurements of 7 ppm metal solution over a 4-hour period using an untreated river water sample. This series of 60 successive runs yielded a relative standard deviation of 1.2%. This indicates that constituents of the natural water sample do not foul the surface, in the short term.

The device responds favorably and rapidly to sudden changes in the metal concentrations level, with no apparent carry over. The lack of memory effect was assessed upon switching between 3-ppm, 10-ppm, and 3-ppm metal solutions. The response decays sharply upon placement in the 3-ppm metal solutions, and rises sharply upon returning to the 10-ppm solution. Such dynamic properties indicate great potential for providing alarm and warning capabilities. Monitoring frequencies as high as 2 runs per minutes are attained in connection to the fast square-wave scanning.

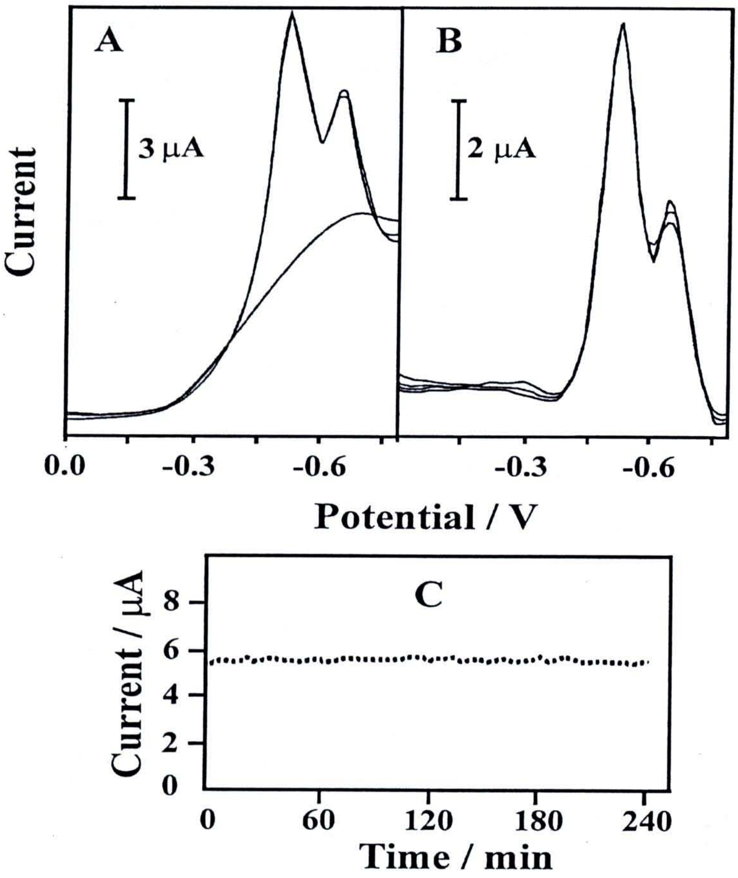

Figure 3.7 Response of the remote carbon-fiber submersible probe to the 15 repetitive measurements of 2 ppm metal solution using conventional (A) and subtractive (B) voltammetric mode along with the resulting stability plot (C).

The above experiments illustrate that trace (ppb and ppm) levels of heavy metal concentration can be monitored continuously and rapidly at large sample-instrument distances by coupling subtractive square wave voltammetric method with a newly designed compact remote probe. The new monitoring capability is characterized with high sensitivity, speed, simplicity, reproducibility and stability for heavy metals. The device responds rapidly and reversibly to sudden changes in the levels of the metals. However, the measurement of some metals will require the removal of oxygen from the samples to provide selectivity and sensitivity.

3.4 NPRU Sensor Performance

Major attention was given to the optimization of variables of the square-wave waveform (including the frequency, potential step, and amplitude) essential for attaining high speed without sacrificing the sensitivity. A computerized baseline subtraction was developed to compensate the oxygen background contribution and hence to facilitate the detection of low ppb levels of metal (see Figure 3.8). The optimal device offered high sensitivity and selectivity, fast response, excellent precision/stability, and absence of matrix effect, and hence meets the demands for underwater sensing of metal. A typical stability data involving 30 repetitive runs of 3 ppm metal solution are displayed in Figure 3.9. As indicated from Figure 3.9, such series yielded a highly stable response with a relative standard deviation of 2.19%.

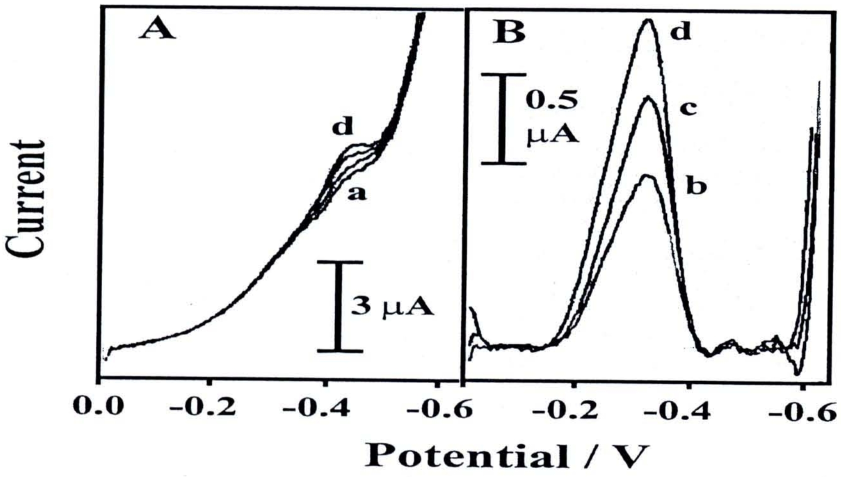

Figure 3.8 Square-wave voltammograms for background (A, a) with the increasing levels of metal in 20 ppb steps (b-d) without (A) and with (B) background correction.

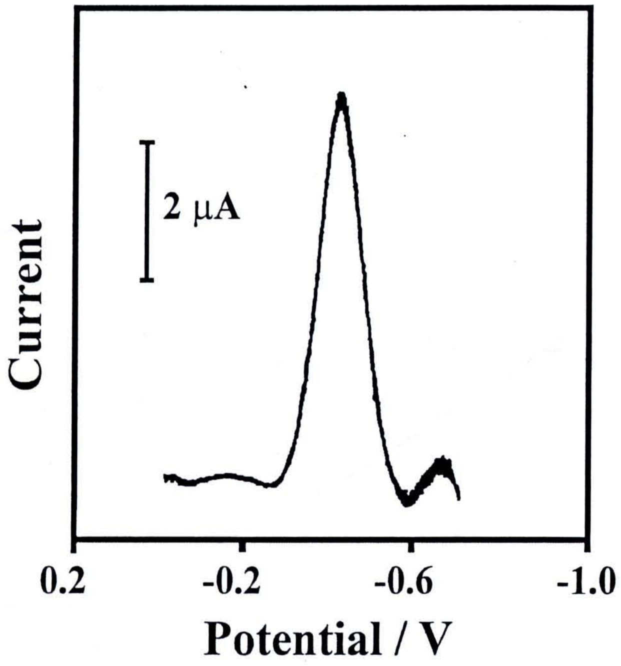

Figure 3.9 Stability of 30 repetitive measurements for 3 ppm of metal solution at submersible carbon fiber based electrode assembly.

3.5 Concluding Remarks

The examples described in this chapter illustrate the power and versatility of modern electrochemical devices for detecting metals. These developments would allow field testing for heavy metals to be performed more rapidly, sensitively, inexpensively and reliably, should greatly facilitate the realization of *in-situ* detection of heavy metals. The resulting *real-time* monitoring capability should thus have a major impact on the way that metals are monitored and upon the prevention of environmental pollution.