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Real-time Detection of Cyanide in Surface Water and its Automated Data Acquisition and Dissemination System

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ABSTRACT

Use of cyanide in developing countries is rampant, especially in gold mining areas. Though it could cause serious environmental problems, cyanide contamination is of less priority for government monitoring because of the limited resources. The current detection and monitoring schemes of cyanide are the conventional and expensive laboratory-based methods, which need technical capabilities to conduct the actual testing and preparing manual data recording, making it tedious and too laborious. More efforts were directed towards digitizing the data recording from manual laboratory analyses as the manual data recording usually cause problems like delayed information, lost data, and erroneous data entry. Hence, the goal of this study is to provide a cost-effective and zero manual-recording measurement method for cyanide in water samples. This work focuses on the design of electrochemical measuring device with the same capability with the portable or benchtop-type of cyanide meter but with an automated and real-time data recording using global system for mobile communications (GSM) technology. Results of this study showed that with the existing GSM technology and infrastructure of the new monitoring system, the measurements are comparable to that of a commercial bench-type cyanide meter with an R-squared (R^2) of 0.9907. It was also noted that data being recorded were intact during wireless transmission testing using the GSM Network. The results obtained suggest that wireless communication using GSM Technology could be applied to environmental monitoring. Importantly, the new developed online system for cyanide monitoring offers significant advantages over the conventional techniques such as low-cost, easy deployment, and ease of use. It can increase spatiotemporal data for better analysis of the data. The automated data acquisition and display through cellular phones are also made readily-available.

INTRODUCTION

Human beings are aware of cyanide toxicity since early civilization. Cases of cyanide exposures in the Philippines, a developing country, have been reported (Stark et al. 2006). In developed countries, the cyanide disaster is well documented especially in the mining industry in which tons of cyanide were accidentally released to rivers, lakes, and oceans (Mudder et al. 2004). The need for more programs related to cyanide detection, monitoring, and fast information dissemination should be done to curtail more cyanide-related incidents.

Cyanide detection and monitoring are essential because of its toxicity to human beings and other living organisms (Ramzy 2014). Although nature produces cyanide through cyanogenic glucoside through plants, it is mostly man-made and intended for industries ranging from metal mining to medicine (Barnes et al. 2000). Cyanide toxicity is associated with various accidents, human diseases, and deaths (Guimaraes et al. 2011, Holden 2015).

Because of cyanide's toxicity and the possible damage, it could bring to humanity, several methods were developed to detect and monitor its presence. Some research deals on how to mitigate the effect of cyanide released to the environment (Gacsi et al. 2005). Despite these previous efforts, some researchers continue to pursue and explore the improvement of cyanide detection methods, protocols, and implementation. Most of these researches focus on increasing the frequency of data sensing by using mobile vehicle (Demetillo & Taboada 2019), lowering the cost to encourage implementation of monitoring and detection especially in developing countries (Nemiroski et al. 2014), improving information dissemination, effective methods of continuous monitoring, and other enhancement opportunities. Some

conventional methods involve atomic absorption spectroscopy (AAS), voltammeter (Safavi et al. 2004), titrations, high-performance liquid chromatography (HPLC) (Gamoh 2002), ion chromatography (IC), amperometry, polarograph, ion-selective electrodes (potentiometry), and fluorimetry. There are also new methods developed for cyanide detection which include electrochemical detection (ECD) (Abbaspour et al. 2005), optical sensors, gas chromatography (GC) (Gambaro et al. 2007, Murphy et al. 2006), quartz-crystal microbalance (QCM) (Sun et al. 2005), and mass spectrometry (MS). These traditional and new methods which mostly involve tedious laboratory analysis are also only capable of detecting low-level cyanide content. While these methods are accurate, they however, still have many limitations ranging from large sample size requirements, long detection period, limited frequency (limited information), and few sampling places (more sampling places increase cost). Analytical methods are also in need of expensive laboratory with high-end instruments, labor-intensive, and require highly skilled and specialized personnel, where scarcity of numbers exist in developing countries.

Cyanide concentration profile and distribution varies because of some environmental factors; thus, a need for real-time analysis is highly desirable. With much of the affected areas being far from the laboratory and considering the time of travel, it is difficult to get the real-time scenario of cyanide level especially rural and far-flung areas. Besides, the information provided by conventional off-line techniques cannot give managers and authorities, the lead time needed for mitigation measures in case of some accidents. Moreover, dynamic information through real-time data as updates and input to decision making and planning is vital for researchers, environmental managers, and other stakeholders (Bokingkito & Llantos 2017). With these, there is a need for fast and accurate acquisition of data, and it is reasonable to design alternative solutions, which could monitor the dynamic changes of cyanide concentrations in real-time. The automated detection system replaces the conventional laboratory-based cyanide detection methods because of several drawbacks like complexity, high-cost and slow information dissemination (Reddy et al. 2017, Gillooly et al. 2019).

Nowadays, the electrochemical technique has been the driving force for the continuous development and enhancement of cyanide monitoring (Jackson & Logue 2017). Advances in electronics, mobile communication technology, smartphone technology, and open source software served as enabling tools in the development of enhanced-sensing instruments. Improvement in electronics, in both size and capability, makes the new electrodes more low-cost, with the capacity for faster *in-situ* analysis, easy

to prototype and deploy (Mross et al. 2015, Qin et al. 2018, Xu et al. 2016, Zhou et al. 2017). However, much of the improvement focused on the enhancement of the electrode (Ma & Dasgupta 2010) and very few for a complete system or set-up for automated cyanide monitoring (Randviir & Banks 2015).

This study aims to design, develop and implement real-time detection of cyanide in surface water and its automated data acquisition. This enables for faster information dissemination of the cyanide level of an area and automation of data recording which eliminates error caused by the manual methods.

MATERIALS AND METHODS

Chemical Reagents

All the chemical reagents used in this work were obtained from Hannah Instrument (USA). Deionized water, ionic strength (pH) adjuster (HI 4001-00) and dried KCN salt were mixed for the preparation of the standard solution. The cyanide electrode was filled with a reference fill solution (HI 7072) before starting new measurements based on the standard procedures in using ISE.

Apparatus, Electronics Components and Software

One of the most common methods in cyanide detection is using the commercial benchtop cyanide ion-selective electrode (ISE). The utilization of the customized electronics circuit and its ability to perform automation, especially in data acquisition, makes this research unique compared with the existing methods.

A commercial benchtop cyanide meter (Hannah Instrument-USA) serves as a reference method to validate the accuracy of the newly designed system. Both the methods, reference and the new system, employed a combination type of ion-selective electrode (ISE) from Hannah Instrument. This type of electrode is known for its easy usability and cost-efficiency compared to using two or three electrode systems.

The primary purpose of the interface circuit is to link the microcontroller and the ISE and condition the signal generated from the ISE as an input signal to the microcontroller. It is a customized circuit which consists of instrumentation (Philips, Japan) and an operational amplifier (Motorola, USA).

The microcontroller is an Arduino Mega 2560 (Arduino, Italy). Wireless communication transmitter and receiver (transceiver) is a GSM/GPRS module from Arduino (Italy). The system relies on battery as a power source with a lithium-ion battery (Panasonic, Japan) as the preferred battery type
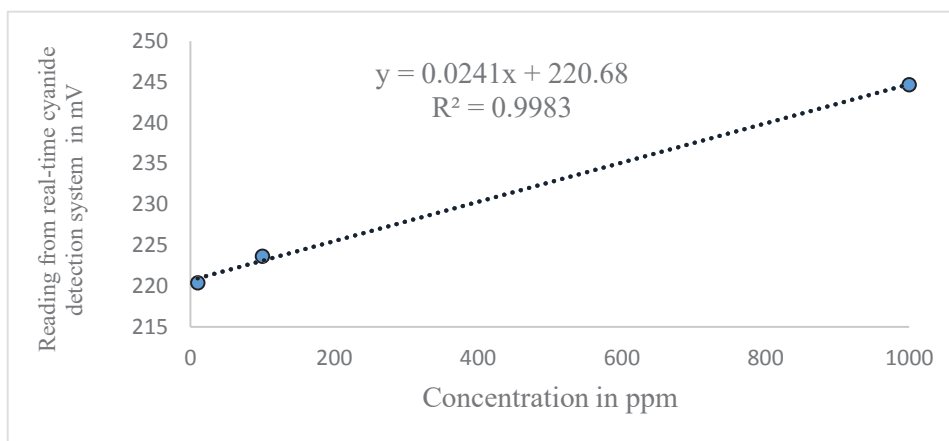
Fig. 1: Calibration curve of the cyanide sample.

for its high-energy capacity. It also has a timer circuit for its energy management, battery booster circuit and data backup circuitry (SD Card). Results generated from the new system are sent to a pre-defined cellphone (any cellphone type) using any GSM technology like 2G, 3G and 4G.

Arduino integrated development environment (IDE) is the software used for the development of the system's programs like pre-processing and conversion of signals from analog-to-digital and vice versa. Microsoft Excel VBA programming was employed to develop a tool to facilitate downloading of data from cellphone and SD card to a computer system for data banking and additional processing purposes.

Electrochemical Experiments

ISE calibration: The direct calibration method was adopted for the preparation and calibration of the cyanide ISE. A series of CN^- standard solutions with a concentration range from 0.1 ppm to 100 ppm were prepared, and the actual cyanide concentration reading (ppm) was measured using the cyanide ISE. Automatic offsetting by dipping the electrode to the prepared cyanide solutions with concentrations ranging from 0.01 to 100 ppm CN^- was conducted. Benchtop meter was calibrated using the cyanide ISE in a concentration range of 0.1 to 100 ppm. Fig. 1 is the calibration curve of cyanide sample. This graph is linear and highly reproducible which indicates good correlation with the standard samples.

Quality control: To confirm the validity and the performance of the newly-designed system, several electrochemical tests were conducted using the commercial bench-top cyanide meter and the new system under the same condition. Real water samples from the creek taken in a 15-minute interval were tested alternatively using the cyanide ISE and the newly-designed system utilizing the same electrode. Several samples were tested for its accuracy like combining water

samples taken from a different location with the addition of the ionic strength adjuster (ISA) at 1000, 100 and 10 ppm.

Sampling Site

The sampling site is the creek running within the Caraga State University campus. The samples were taken at the various locations of the creek.

RESULTS AND DISCUSSION

Introduction to the Design of the System

Systems overview and design: Fig. 2 shows the block diagram of the overall system. It includes a commercial ISE as an electrochemical sensor to detect and monitor cyanide, a customized interface circuit, a controller, energy source, and the wireless transmission system. It also included other necessary electronics peripherals like a timer circuit, battery energy booster and back-up memory (SD card). The ISE through the interface circuit connected to the microcontroller using the I2C protocol. The electrode is a commercial ISE subjected to an international standard calibration and testing. Availability and easy acquisition for future implementation was also a reason for selecting the ISE based on the study (Hu et al. 2016). A customized interface circuit was designed and implemented to facilitate detection even with a small concentration of cyanide and to condition it for microcontroller input. The microcontroller preprocesses the signal into information (value of cyanide level in terms of mV). Before sending the newly processed information to the transceiver, the microprocessor converts the information into a suitable format ready for transmission using the GSM transceiver module. The receiver sent the information to the pre-identified cellphone users or computer systems. Backup information saved in the SD Card (attached
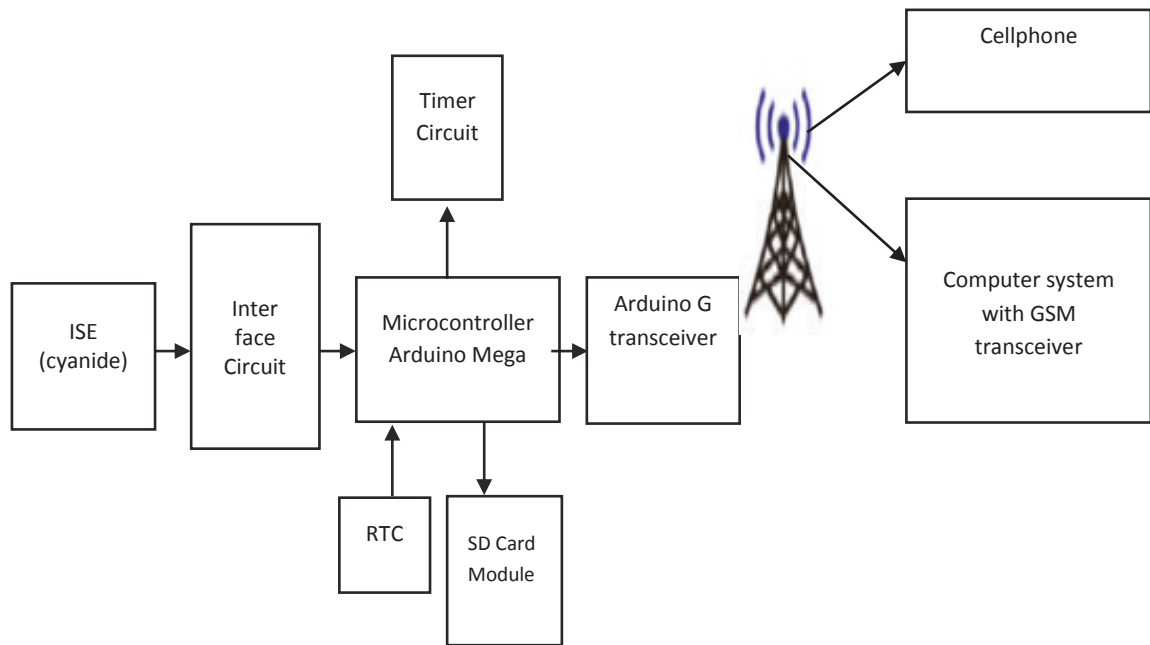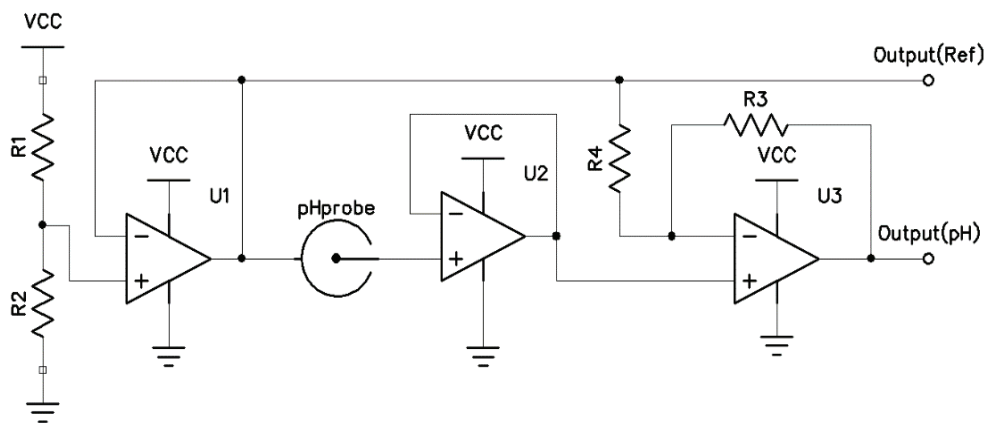
Fig. 2: Block diagram of the overall system.

Fig. 3: Schematic diagram of the interface circuit.

to the microcontroller) can be retrieved anytime if the need arises.

Circuit system: The primary circuits of the system are the interface circuit, a microcontroller, the energy source, and management system, the wireless communication systems and other peripheral components like the SD card and real-time clock.

The customized interface circuit is based on the requirement of detecting ionic concentration which is a high input impedance. A schematic diagram of the interface circuit

is shown in Fig. 3. ISE produces a small signal based on the cyanide level of the samples which the microcontroller cannot read directly. The primary function of the interface circuit is to boost and condition the detected cyanide level to be compatible with the microcontroller.

The microprocessor coordinates all the operations of the system. It preprocesses the gathered data into a usable format. Another function of the microcontroller is to prepare the signal for long-distance transmission using the wireless transceiver. The microcontroller is an Arduino Mega 2560. It

is one of the latest among Arduino development board. One of its features is the presence of an ample number of analog and digital (18) input pins for future expansion.

The timer circuit is an essential circuitry for power management. It allows the system to go to a sleep mode or wake-up mode on a prescribed time, and signal the ISE to gather data again thus, saving the much-needed battery energy and in effect extending the lifespan of the system. Another circuitry is the SD card module which hosted the micro-type of an SD memory card and served as the primary backup of the whole system. It is a backup mechanism that triggered every time the sensor-transmitted data or information. The format of the backup data is customized to fit the base station database format for easy transfer and retrieval of backup data if needed.

To energize the sensor, a lithium-ion battery with a capacity of 4350 mAh/3.7V was used. Within the sensor unit, some electronic components need up to 5 volts for their operation like the GSM module, which is an energy booster installed as part of the sensor component.

The GSM transceiver is a commercial GSM/GPRS module used to send data to a base station or directly to a pre-identified cellphone number. It can also receive SMS from the remote station for utilization during unscheduled data gathering, maintenance purposes, and others. The wireless transmission also used GSM/GPRS module which utilizes the commercial telecommunications infrastructure for the transmission.

Calibration: Before using the electrochemical probe (ISE), standard calibration sample with cyanide solutions was maintained at room temperature and stirred continuously. Calibration measurements were made with 100 mL of test solution in a suitable Pyrex beaker. All glassware was always decontaminated and washed several times with double-distilled water (DDW). Cyanide standard solutions were prepared using DDW and ionic strength (pH) adjuster (10-mL of HI 4001-00).

ISE characteristics and features: This work utilizes the ISE (HI4109) from Hannah Instrument (Rhode Island, USA), which is a solid state combination ion-selective electrode (ISE) for the determination of cyanide (CN-). The output of the ISE is a potential difference due to changes in the sample's ionic activity. Typically, ISE parts comprise of the following (i) connector to readout circuit or meter, (ii) cap, (iii) sensor body, and (iv) the sensing membrane. Protection was provided to the sensing element of the electrode by the polyetherimide (PEI) body, being the most sensitive part of the electrode and where accuracy and sensitivity set within its small and sensitive circuitry. It has a detection limit from 0.026 to 260 mg/L CN-.

Evaluation of the efficiency of the electrodes was conducted by comparing the specifications from the manufacturer (Hannah Instrument) to the actual output during the actual determination of cyanide in the laboratory or field. Also, this company specification serves as the reference in terms of the limits of detection, slope, response time and long-term stability as essential parameters to measure electrode performance. Calibrations are conducted using the manufacturer's manual of operation.

The potential response from the two testing additions of ionic strength adjuster (ISA) was linear. Tests with only fresh-water samples (no mixing of ISA) show an erratic reading except for the 1st reading which shows an accurate measurement. The potential drift was approximately 20 mVh^{-1}. The response time of the ISE is approximately 10-20 seconds.

Repeatability and Accuracy of Cyanide Detection and Monitoring

In establishing the validity of the research methods, a standard sampling solution was tested by both the systems (new and a commercial benchtop meter) using the same electrodes resulting in a high R-squared value which constitute to a good accuracy of the new systems. To check the validity of the proposed method, measurement of the prepared cyanide standards solutions was made using the cyanide ISE (as the reference method) and the newly-designed system. The results of the analysis suggest that there is a higher correlation (high R^2 value) of the obtained results between the cyanide ISE method and the proposed method resulting to high R^2 value which constitutes to a good accuracy of the new systems. The results of the analysis suggest that there is a higher correlation (high R^2 value) of the obtained results between the cyanide ISE method and the proposed method.

Fig. 4 depicts the results obtained from the measurements of a mixed standard solution and the real samples. The results show that the recorded potential (200 mV) in a solution with a known cyanide concentration is in good agreement for both the applied methods. This further suggests that indeed, the newly-designed system is able to detect an accurate measurement in the manner as the cyanide ISE technique. However, it was observed that for water samples the potential reading was slightly higher using the cyanide ISE as compared to the newly-designed system. The reason for the observed nonconformity of results may be due to the effect of the ionic nature of the real water sample. For water samples, the values obtained through the commercial bench top tester was observed to be higher than those measurement readings from the new system.

Fig. 4 shows the results of twelve different setups consisting of 7 sampling sites. Data show that results from the
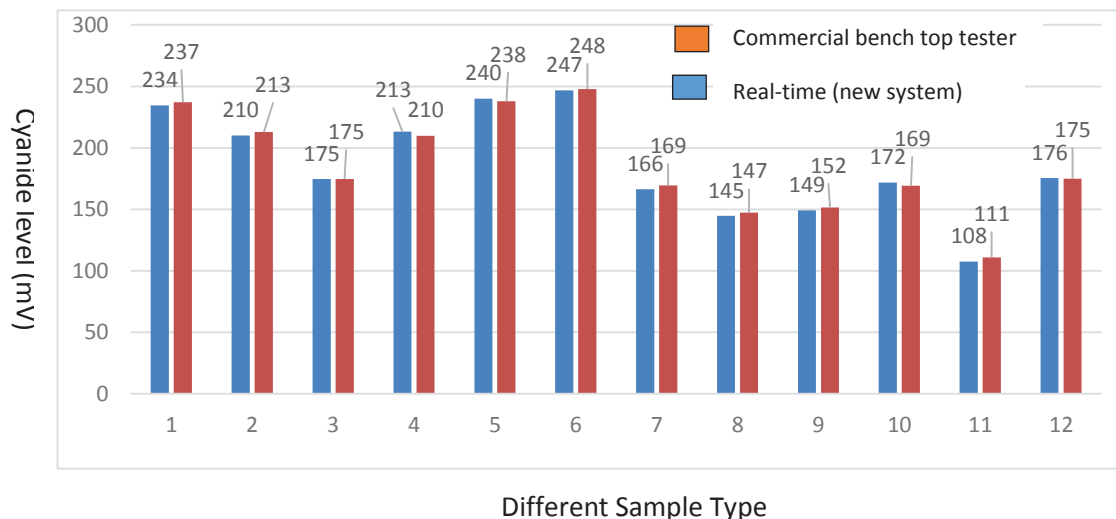
Fig. 4: Results obtained from the measurements of a mixed standard solution and the real samples.
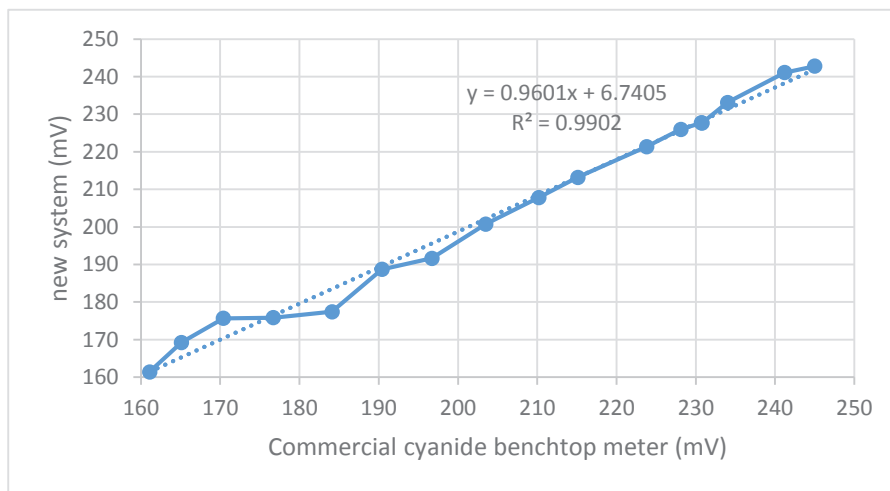

Fig. 5: Results generated from the new system with an R^2 of 0.99.

commercial benchtop meter are almost the same with the results generated from the new system with an R-squared of 0.99 as shown in Fig. 5. The average of the difference between the results of the ten samples is approximately 2mV. The lowest of these differences is 0.07 mV, and the highest is 3.35 mV. It shows that the newly developed system is capable of detecting cyanide at par with the commercial techniques available with an additional capability of automated data acquisition and reporting using GSM technology.

Fig. 6 shows the results of testing wherein the samples are tested without ISA. As expected, sample has erratic and unstable results. Fig. 7 shows the results of the testing where-in the required water samples and ISA are mixed (standard method) and resulted in stable readings.

In this work, the demonstration of the accuracy and suitability of an automated detection with real-time data acquisition and reporting prototype using ISE and wireless communication technology performed using a prototype is reported. A good correlation ($R^2 = 0.99$) between the levels determined by the accepted reference method (benchtop meter) and those measured by the new system were obtained and with no observed systematic errors.

CONCLUSIONS

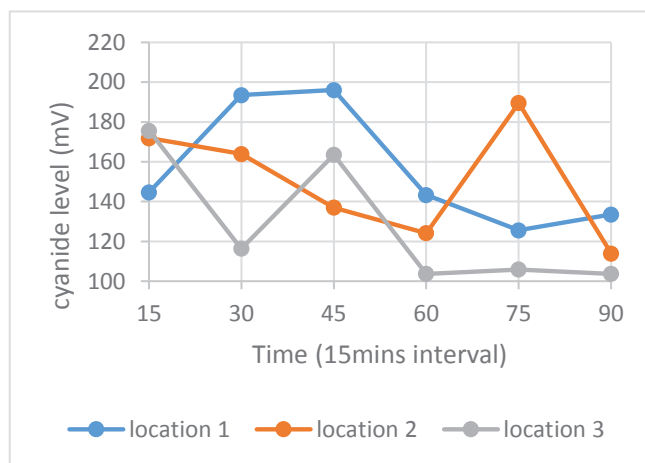Cyanide concentration can be monitored in real-time from

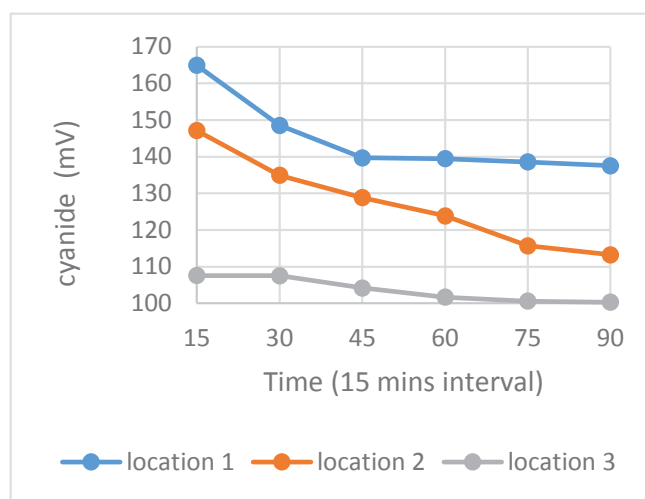Fig. 6: Results of testing wherein the samples are tested without ISA.

Fig. 7: Results of the testing wherein the required water samples and ISA are mixed (standard method).

the actual site and data can be transmitted immediately to the intended user's cellphones display or a centralized database system. The new system offered advantages like reduction of cost in doing multiple sampling and lesser resources both technical personnel and equipment, fewer chances of human error during the manual recording, and fast information dissemination using cellular phone technology.

Finally, the study provides proof of concept in automating the cyanide detection, analysis, and dissemination using customized circuit, electrochemical analysis, and open source software. The new system can perform the task of the commercial portable cyanide meter at a much-reduced price. It also addresses the issue of erroneous manual data recording through automated wireless transmission of data to an intended user-cellphone or computer systems. These advantages could encourage individuals, government agencies, researchers and other stakeholders from developing countries to perform cyanide monitoring in water bodies of their respective areas.

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