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PC BASED AMPEROMETRIC ANALYSER

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A PC based instrument was developed to carry out amperometry, one of the important electroanalytical techniques Salient features of the instrument along with the experimental results and illustrations depicting hardware and flow charts of software are presented.

Key Words: PC, Amperometry and Electroanalytical technique.

INTRODUCTION

A PC based amperometric analyzer has been developed to carryout BOD (Biological oxygen demand) / DO (Dissolved oxygen) measurements. Amperometry, the incorporated analytical technique, enables the PC based analyzer when coupled with a biosensor to carry out BOD/DO analysis in the industrial effluents in ppm level. This instrument, by measuring BOD/DO in the industrial effluents, can play a vital role in the field of pollution monitoring and control to assess the rate of pollution in and around the process industries such as food industries,, sugar and distillery units and dairy units etc.

Amperometric detection technique is one of the analytical techniques commonly employed to measure concentration of organic compounds. Amperometry is normally carried out in stirred or flowing solution at a rotated electrode. Current is measured as the compound undergoes oxidation or reduction at the working electrode held at a fixed operating potential. Amperometry is a potentially controlled analytical technique, which enforces and maintains a predetermined potential of a working electrode of an electrochemical cell against a reference electrode and the cell current is monitored as function of time. Amperometry has been found to be an important electrochemical technique. Besides being simple and elegant, combined with advanced signal conditioning techniques to probe process currents to the tune of nano-amperes, it has proven to be quite useful in implementing PC controlled analytical instrumentation based on bio-sensors for BOD/ DO measurements. In the case of amperometry, the working electrode is maintained at a constant potential such that the ionic species of interest get discharged at the electrode. The resulting cell current is a measure of concentration of the ionic species, which in turn is the indication of BOD concentration.

This paper describes with suitable illustrations about the developed personal computer based Amperometric detector, which can be used to measure the concentration of BOD/ DO using a biosensor. This PC based instrument can have extended facilities such as an on line monitoring of BOD / DO of any organic compound in any of the above said places coupled with a biosensor. This instrument has been designed to have operational sensitivity to concentration level ranging from 1 ppm to 60 ppm.

BOD

Biological oxygen demand is (BOD) is an important and useful indicator of the total amount of organic pollutants present in waste water. The BOD is defined as the quantity of dissolved oxygen required to completely oxidize all assimilable organic compounds present in the water sample by the micro organic organisms under defined experimental conditions. The BOD is of special importance in the assessment of polluted surface water and waste water. Its application is indispensable as in laying out data during the construction of sewage works and project comprising of effluent treatment plants and other plants to provide effective pollution control. In addition, the fermentation industries need the estimation of various organic compounds present in the process stream to control the process. For this, bio-chemical oxygen demand (BOD) is an important parameter in estimation of organic content in industrial

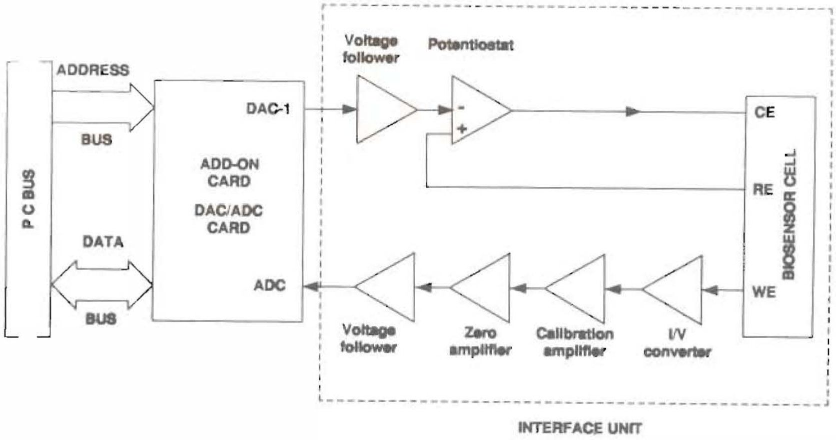

Fig.1: Funtional Block Diagram

effluents. By estimating the exact amount of organic material in waste water, an efficient treatment can be adopted.

Bio-chemical oxygen demand is a measure of oxygen required for the bio- chemical oxidation of organic matters by microbial. By measuring dissolved oxygen (DO) in waste water, indirectly the amount of organic compound in the water can be calculated. Estimation of BOD by conventional method requires five days incubation period and skilled technicians are needed to get a reliable estimate. Moreover a large storage facility is needed to store waste water for treatment before discharged. The bio-sensor interfaced with the instrument requires only 5 minutes to estimate the BOD, which has been developed at EEC division, CECRI.

EXPERIMENTAL

Hardware description

The following are the main components of the instrument:

1) A PC AT
2) ADD-ON card. and
3) Interface unit.

The components of the hardware incorporated in the interface unit, as shown in fig 1, comprises a voltage follower, potentiostat, I/V converter, calibration amplifier, and off-set control. The current due to electrochemical reaction in the cell is in the order of nano amperes. The amperometer is a precision hardware to provide noise free measurement of very low current in the order of nano amperes. In the case of electrochemical biosensors, the transducer converts the chemical species generated by the biochemical system into electrical analog signal. This instrument coupled with the biosensor senses the current induced in the working electrode by maintaining the working electrode potential with respect to the reference electrode with the aid of the potentiostat incorporated in the interface unit. As the current is very low in terms of nano amperes and is directly proportional to the concentration of BOD in ppm units, the instrument with suitable hardware comprising high precision operational amplifiers configured as potentiostat, I/V converter and calibration amplifier convert the induced current suitably to a voltage level proportional to the measured concentration of BOD in ppm units.

The design of potentiostat and I/V converter was based on high precision operational amplifier OPA 111 (Burr-Brown) which finds its application in bio-medical instrumentation. The block diagram as depicted in the Fig. 1. describes essential components of the PC based instrument. The high precision operational amplifier. configured as potentiostat in the interface unit connected to the add-on card hooked up to the PC bus of the computer, maintains the potential set through the DAC channel of the A / D - D / A card, while the low current induced in the bio- sensor cell as a result of the applied potential, is converted into voltage level by the operational amplifier which functions as an I / V converter. Zero amplifier introduces voltage offset to the output signal connected to the AD channel of the add-on card, and the calibration amplifier enables suitable amplification so as to enable it to be in the measurable range of the (data acquisition card) A / D channel of the add-on card.

The amplified and processed analog signal is converted into the digital signal by the on board ADC of the ADD-ON card, which is interfaced, with the PC. The ADC, (AD 574) in the ADD-ON card is a complete 12 bit A/D converter. The Block diagram as shown in fig.1 represents the PC based

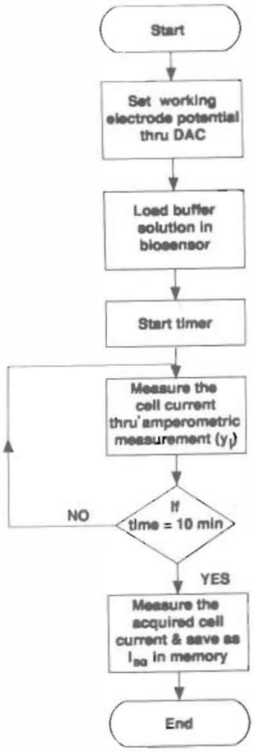

Fig.2: Background current zeroing

TABLE.1: Comparison of BOD obtained from 5 day method and amperometric measurements

Sample	BOD 5 day method (ppm)	Instrument read-out (ppm)	
		ppm	nA
Synthetic BOD mixture	250	221	60
Paper and pulp untreated sample (100 times diluted)	56650	85000	85
Paper and pulp (Treated Output without dilution)	8.6	11	8
Sewage	22	17	9
Distillery waste of Glucose Industry			
(i) Sample from collection tank (10 times diluted)	11112	10620	228
(ii) Sample from Aeration tank (without dilution)	40.82	36.60	68

amperometric analyzer. By using the Add-on card interfaced with PC the working electrode potential of 600mv required to be applied to the bio-sensor cell is set through a control software sub-routine driving the DAC with appropriate 12 bit digital data. The amount of current induced in the Biosensor is converted into its equivalent voltage with suitable gain introduced in the feed back of the I/V converter. The amplification factor of the calibration amplifier is so chosen that 1mV of the final output potential of the interface unit to be equal to 1 nA of the cell current induced in the bio-sensor. Buffer amplifiers introduced in the initial and final stages of the interface unit are to provide impedance matching between the add-on card. The add-on card has eight A/D channels with a data conversion time of 25 microseconds per channel. The analog input range of the A/D - D / A card is 0 +/- 5v.

The following are the specifications of the developed instrument:

1. Sensitivity to measure cell current :±1nA
2. Cell potential range : +5v to -5v with 2 mV accuracy
3. Cell current acquisition time : 25µs
4. Read out Response time : 1 mSec(limited to that of the bio- sensor)

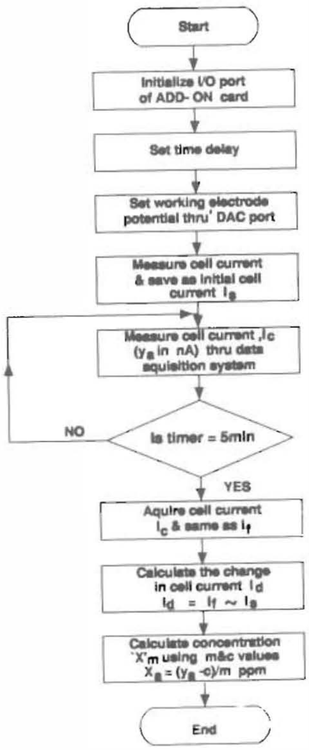

Fig.3A: Cell current Measurement

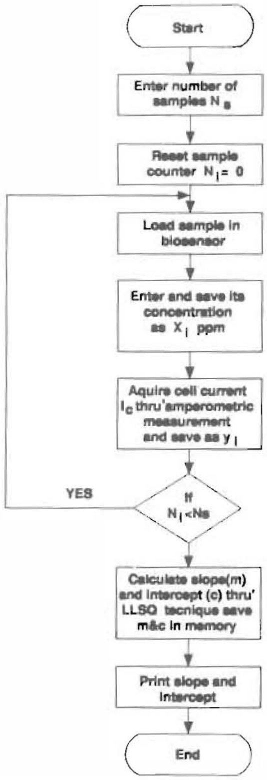

Fig.3B: Calibration

Software description

The user interactive menu driven software program written in "C" language was incorporated with several sub-routines to carryout all the functional modes of the instrument. The Software for the developed instrument comprises several software subroutines to execute all functional modes of the instrument such as "Background zero mode" as shown in the Flow chart (Fig 2), "Measurement mode" and "Calibration mode" as shown in the Flow charts, Fig.3a and Fig 3b respectively. The elegant software package incorporated with an arithmetic software module to perform Linear least square (LLSQ) method as shown in the Flow chart, Fig 4, enables the instrument to perform calibration effectively and its auto zeroing facility provides more accurate BOD measurements.

The functional modes of the instrument are as follows:

1) Background current Mode,
2) Measurement Mode,
3) Calibration Mode

Background mode

In this mode, background current of the buffer solution is acquired and the value of cell current in nA is displayed, where background current is defined as the current flowing with in the three electrode bio-sensor measured against buffer solution free from organic contents. This value of current is called as background current (I) and saved in memory stack.

Measurement mode

It is the functional mode of the instrument which measures the bio sensor cell current and calculates the difference between the background current, I_{BG} and the cell current, I_C. This change in cell current value or this difference value is taken as I_D (I_{BG} ~ I_C), and it is directly proportional to concentration of organic contents of the biosensor electrolyte which is a measure of BOD of the sample solution. In this mode the value of this cell current, I_c, is displayed in nA and by using the values of slope (m) and intercept (c) obtained in calibration mode, BOD/DO concentration value of the unknown samples are determined and displayed in ppm units

Calibration mode

In this functional mode, with a set of solutions of known concentration values in ppm units, the instrument is calibrated by means of the calibration software subroutine. The calibration subroutine performs a series of sample solution current measurements, each against their respective concentration values entered by the user and saved in memory locations. It proceeds upto the total number of samples, n, as entered by the user. After having obtained cell current values and stored in memory locations against their known concentration values, an arithmetic software subroutine to implement Linear Least Square (LLSQ) Technique is executed to obtain the slope (m) and intercept (c) values which are the parameters of straight line equation. Thus the calibration mode determines the values of slope and intercept, with which the instrument is ready to measure concentration of unknown samples.

The LLSQ technique

For any unknown sample solution, the instrument first carries out amperometry as a result of which the value of change in current, I_d, is obtained. If it is current measurement mode, this value is directly displayed through the display routine. In the case of ppm readout mode, using multi-byte decimal arithmetic routines and employing the parameters of straight line equation such as slope (m) and intercept (c) obtained through calibration the unknown concentration in ppm units is calculated after measuring the cell current through amperometry as follows.

$$Y = mX + c \quad (1)$$

$$X = Y - \frac{c}{m} \quad (2)$$

Where X is the unknown concentration, m=slope, c=intercept and Y is the value of cell current in nA measured against the sample solution of unknown concentration.

Calibration mode is enabled through keyboard interaction routines necessarily required to enter n, number of samples of known concentration, and concentrations (Xi to Xn) in real ppm units against amperometric measurements of cell current (Yi to Yn) calibration mode further proceeds through execution of arithmetic routines to calculate and determine the values of slope and intercept form the formulae as given below.

$$\text{Slope, } B_0 = \frac{\Sigma (X_i - X)(Y_i - Y)}{\Sigma (X_i - X)^2} \quad (3)$$

$$\text{Intercept, } B_1 = Y - B_0 X \quad (4)$$

with these values of slope and intercept obtained and saved in respective memory stacks, the instrument remains calibrated and become ready for measuring BOD of samples of unknown concentrations. Thus with the elegant and powerful software package which plays vital role in all automatic data acquisition and control systems, the PC controlled BOD/DO analyzer coupled with the microbial based biosensor ably provides BOD measurements.

RESULTS AND DISCUSSION

After calibrating the PC based analyser coupled with the biosensor, amperometric measurements over a set of unknown samples collected from different industrial effluent treatment plants, were carried out. In Table I, the readings obtained are displayed against the readings obtained in conventional 5 day incubation method.

The tabulated readings as shown in Table I, indicate that there is a good agreement between the measurements obtained in both the amperometric and 5 day methods. And with its versatile hardware and software package, the developed PC based analyzer coupled with a microbial biosensor is found to carryout BOD measurements accurately.

With suitable incorporations in the hardware package the instrument can provide on-line monitoring of BOD/DO in the effluents of various process industries such as paper & pulp, sugar, food processing, distilleries, dairy and sewage treatment plant.

CONCLUSIONS

The following are the main conclusions:

* The developed PC based instrument provides direct display of BOD/DO in ppm level i.e. no graphical analysis is required to obtain BOD/DO concentration.
* Response time is as fast as that of the Biosensors.
* With suitable software and hardware the system can function as on line BOD monitor with data logging instantaneous display of background current, sample current and ppm is possible.
* Inbuilt 5 minutes timer by which by every 5 minutes, the background current, and sample current will be saved in memory and can be displayed.
* On line monitoring is possible.
* Auto zeroing facility.

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