Proposed Method for Modern Voltammetric Studies

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Abstract

Acquiring more and more physical comforts for the people has been the accepted goal for prosperity and development of the society. India, being a developing nation, has undergone rapid industrialization in the last few decades. With the enormous growth and expansion of technology, a serious problem of environment pollution has cropped up, which has now become a big threat for vegetation and animal life. Among its various forms, soil pollution is probably the worst as this is related to our food. Industrial waste effluents contain a number of toxic metals and organics which are hazardous to soil and vegetation. Soil is also getting polluted due to day by day increasing use of pesticides. Voltammetric methods have proved to be highly sensitive, reproducible and versatile for carrying out trace analysis of metals in diverse matrices.

Key Words: Polarograms, Voltammetric methods, Intercept correction method

1.0Introduction: Today's environment is entirely different than the temperate and peaceful environment which used to be there when human life was cheerful, simple and quiet. Now, the world around us, in its material sense and in its value system, is a product of science and technology. In any sphere of human activity or human Endeavour , for example, increase in food production, in energy production , in health and medicine, engineering goods, electronics etc., the development has largely been as a result of improved use of science and technology. A developing country like India will have to undergo the process of development at much rapid rate. With the enormous growth of technology, serious problem of environmental pollution has cropped up. It has its inevitable effects on animal and vegetation. In various forms, cruel hands of pollution are throttling the living humanism. Air pollution, water pollution, land pollution, noise pollution, soil pollution etc., and all cause serious problems resulting in harmful diseases. Among all these, soil pollution is probably the worst as this is related to our food. In fact soil is getting polluted in many folds like particulate matter from air polluted due to industrial gaseous discharges and heavy consumption of petroleum products near highways, industrial waste effluents which get mixed up with the soil, industrial waste water which is used for irrigation purposes especially in desert areas and day by day increasing use of pesticides in agriculture and so on. The industrial wastes contain a number of inorganic and organic substances. Most of these substances are toxic for vegetation and animal life consequently, an irreversible loss to soil and vegetation qualities results in the long run.

Soil scientists have calculated that soil's fertile layer has been destroyed on two thousand million hectares of land. Environmental scientists also tell us that each year; the industrial plants have been discharging more than 30,000 million cubic meters of untreated water, 250 million tons of dust and 70 million tons of poisonous gases. Inorganic substances present in the industrial waste effluents contains a number of metals like copper, molybdenum, zinc, selenium, arsenic, nickel, cobalt, mercury, chromium, vanadium, lead, cadmium etc. some of these trace elements which are essential for growth and better yield of the food products include copper, molybdenum, zinc, selenium, nickel, cobalt, chromium. To increase the production of crops, number of nitrogen, phosphorous and potassium containing fertilizers are being indiscriminately used now a days. No doubt, quantity wise production has much increased in this way but with the use of these NPK fertilizers, soils and plants have

gradually become deficient in micronutrients and less resistant to pests and other diseases, resulting in a decline in the quality of the food products. To combat with the pest and diseases, a number of pesticides are used in a gross amount. Whenever a pesticide is used; only one percent of this pesticide reaches the target, rest 99% gets mixed up with air, water and soil. As these pesticides are usually not biodegradable, their residual amounts persist in soil and water. These pesticides reach the plants either by direct absorption or through soil and thus contaminate food grains, fruits and vegetables. They cannot be removed from the food products by simple washings and get into the animal body making it prey of a number of fatal diseases. Large number of analytical techniques such as x-ray fluorescence[1], atomic absorption spectrophotometry[2], flame photometry[3], chronopotentiometry[4], and neutron activation analysis[5] are available today for trace analysis purpose but factors such as high cost of instrumentation, much time consumption lower sensitivity and lesser reproducibility reduce the efficacy of these techniques in trace analysis. Voltammetric methods have proved to be one of the most sensitive and reproducible methods available today for carrying out trace analysis in diverse matrices like foods, drugs, plants, soil, water etc.

There are two big industrial areas around Jaipur viz. Sanganer industrial area and Vishwakarma industrial area. Sanganer is well known for its dyeing, printing and washing industries. Waste effluents of these industries contain a number of inorganic and organic substances which reach surrounding fields and pollute the soil and vegetation. On the other hand, Vishwakarma industrial area is a huge area which is having different types of chemical, pharmaceutical, drug, food, petroleum, and textile and alloys industries. Effluents of these industries are continuously polluting the surrounding areas and agricultural fields near to the industries.

Hence it was undertaken to analyze soil and plant samples of the fields surrounding these industrial areas using these modern Voltammetric techniques. Four metals namely zinc, cobalt, nickel and lead were chosen to be determined in these samples. Zinc was chosen because of its ample biological importance to all living organisms. On the other hand, lead is highly toxic and is not required by plants or animals but their concentrations are very low and hence highly sensitive methods are to be used for their analysis. In various crops like sesamum, gram, groundnut, mustard, lady's finger and green vegetables which are grown in agricultural fields of Rajasthan, a number of pesticides such as parathion, aldrin, methyl parathion, endosulfan, monochrotophos, thiram etc. are widely used. Out of these, two pesticides viz. methyl parathion and thiram were selected for quantitative analysis in soil samples. A systematic study of Voltammetric reduction of zinc, lead, cobalt, nickel, methyl parathion and thiram was carried on the various supporting electrolytes under different experimental conditions using various Voltammetric techniques. Results of these investigations were used to develop reproducible and sensitive methods for analysis of metals and pesticides in soil and plant samples. These methods were used to analyze around 50 soil and plant samples collected from the fields surrounding Sanganer industrial area and Vishwakarma industrial area.

2.0Polarographic techniques: There are different types of polarographic techniques some of them are discussed here-

2.1D.C.Polarography: Polarographic is a talented gift from Prof. J. Heyrovsky[6] to the world of analytical chemistry who invented it at the Charles University Prague in 1922. In polarographic technique, a potential is applied between dropping mercury electrode and a reference electrode such as a saturated calomel electrode dipping in a solution containing electroactive species and an indifferent electrolyte to eliminate the migration current. It investigates solution composition by reducing or oxidizing metals, organics and icons at a dropping mercury electrode (d.m.e).

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reference electrode such as a as a saturated calomel electrode dipping in a solution containing electroactive species and an indifferent electrolyte to eliminate the migration current.

2.2Pulse Polarography: This technique is developed by Barker[7] as an extension of his work on alternating current methods. In pulse polarography, as the name implies, the potential is applied periodically during short time intervals. The purpose of using pulse is to decrease the influence of charging/ capacitance current.

2.3Stripping Voltammetry: The general idea of Stripping Voltammetry was given by Zbiden[8] in 1931 who attempted to measure copper electrogravimetrically by plating it on a platinum electrode. Modern stripping analysis had its beginning in the mid 1950's with W.Kemula's development of the hanging mercury drop electrode.

2.4Adsorptive Stripping Voltammetry: In recent years, still greater advancement in stripping analysis has been done. This is known as Adsorptive Stripping Voltammetry[9]. It is an electroanalytical technique in which the analyte is preconcentrated first by absorption onto the working electrode rather than by electrolytic deposition. Subsequent analysis of the absorbed substance is done by scanning the potential towards more negative values.

3.0Quantization Method: For estimation of concentration of an electroactive species using polarographic techniques, by two methods namely absolute method and comparative method are used. In "absolute method" diffusion current constants are used. Its essential characteristics are that different capillaries are used within the unknown and known solutions. And so it involves the errors inherent in the equations describing the relationship between the wave height and the capillary characteristics. This is a less accurate method of quantitative estimations.

In "comparative methods" the calibration data are obtained with the same capillary and under the same condition used to analyze the unknowns. The four comparative methods are generally used

3.1Standard curve method: In this method, polarograms of a number of solutions containing known amounts of the electroactive species of interest are recorded -and their wave heights are measured. These data are used to construct a standard curve that is then used to obtain the concentration of unknown solutions from their wave heights[10]. The polarograms of known and unknown solutions must be secured under exactly identical experimental conditions.

3.2Standard sample method: This consists of measuring the wave heights of a standard sample at the same time that the unknown is analyzed[11]. Comparison of the two wave heights directly gives the concentration of the unknown solution.

$$\frac{Id_1}{Id_2} = \frac{C_1}{C_2} \qquad (1)$$

Where Id_1 – diffusion current of the standard sample solution, Id_2 – diffusion current of the unknown sample solution, C_1- Concentration of the standard sample solution, C_2- Concentration of unknown solution

3.3Standard Addition method: The method of standard addition, which appears to have been originated by Hohn, is most widely used for quantitative estimation of an electroactive species[12]. These are three standard addition methods, all based on the increase of wave height produced by adding a known amount of the substance being determined. In the commonest of them, polarograms of the unknown solution is first recorded and then a known volume of a standard solution of the substance of interest is added to the unknown solution and a second polarograms is recorded. From the increase in current value caused by the known addition, concentration of unknown solution can be computed; using this formula

$$C_u = \frac{i_1 v C_s}{i_2 v + (i_2 - i_1) V} \qquad (2)$$

Where- C_u- Concentration of the unknown solution, i_1- wave height of the unknown solution, C_s- Concentration of the standard solution, V- volume of the standard solution added, i_2- wave height of the solution after adding known amount of the standard solution.

3.4Pilot–Ion Method or Internal standard Method: This method was suggested by Forche[13] is based on the fact that the relative diffusion currents obtained with the equal concentration of various substances i.e. the relative diffusion current constants are independent of the particular capillary that is used provided that the nature and concentration of supportive electrolyte and the temperature are kept constant.

In this method, standard solutions are prepared such that the nature and concentration of both the substances being determined and another substance called the "pilot-ion" despite the fact it need not be ionic and the ratio of their wave heights is measured.

4.0Proposed Method: During the course of trace and ultratrace analyses of metals, pesticides, drugs, dyes etc. being carried in our laboratory, it was observed that nearly all calibration curves give an intercept positive or negative, small or large, depending upon the nature of the voltammogram. On the basis of close and critical examination of these intercepts, shapes of curves and shapes of corresponding blanks, we have been able to propose a new concept of intercept correction. The new method of intercept correction has been proposed. The proposed method is known as Intercept Correction Method. The method has been applied to a number of calibration curves obtained for the analysis of metals and pesticides. It has been found that the errors in these determinations which were between the few percent to 50% without intercept correction were reduced to only ±1.0% in most of the cases after applying the proposed interception correction. It has further been demonstrated the irrespective of the method of measuring peak heights in case of well defined peaks, the error after applying this method of intercept correction were within ± 0.5%.Moreover, in cases, where defined peaks are obtained due to interferences from nature of the blank curve, impurities from the electroactive species of interest, interfering electroactive substances, results within 0.5-1.0%.

5.0Conclusion: This paper is a introduction of the factors that are responsible for soil pollution through which toxic metals and poisonous chemical pass into the food grains, vegetables, fruits etc. and cause hazard to vegetation, animal and human health. This paper also presents the status of Voltammetric methods and quantization methods used for investigation. A new concept of intercept correction has been introduced in this paper.

6.0References

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