

Construction of Multi-Electrodes Electrochemical Detection System for Flow-Injection Analysis (FIA): Application to $\text{Cu}^{1+}/\text{Cu}^{2+}$ Couple

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ABSTRACT

A house-built multi-electrodes detector has been designed for flow-injection electrochemical analysis. The detection system constructed into two parts, the auxiliary electrode (1 mm diameter Pt wire), the working electrodes (5 mm diameter glassy carbon (GC)), 5 mm diameter graphite (GR) and 5 mm diameter poly pyrrole plated (PPPE as conducting polymer) placed in one part where as the reference electrode (Ag/AgCl, sat. KCl) placed in the second part. These electrodes were fitted into a teflon body cell, as it is a good isolator and easy to machine. One can readily change the working electrodes from GC, GR or PPPE without taking the cell apart. The cell based on a conventional laminar flow or on a wall-jet mode of operation. Use of the cell is illustrated by determination of $\text{Cu}^{1+}/\text{Cu}^{2+}$ couple on the different working electrodes. The best results obtained using the conducting polymer with lowest detection limit 10^{-7} M (6.3 ppb as Cu^{+2} ion).

:

$\text{Cu}^{1+}/\text{Cu}^{2+}$

1.0

(GC)

/

(6.3)

10^{-7}

5.0

(PPPE)

PPPE

Wall-jet

(FIA)

(GR)

(Ag/AgCl, sat KCl)

PPPE

GR GC

$\text{Cu}^{1+}/\text{Cu}^{2+}$

.(Cu^{2+})

INTRODUCTION

The concept of FIA was introduced in the mid-seventies by two groups Ruzicka and Hansen in Denmark (Ruzicka and Hansen, 1975), and Stewart in USA (Stewart et al., 1974). The fast and intensive development of the FIA methodology was due to several factors essential for routine analytical determination, such as very limited sample consumption and the short analysis time based on a transient signal measurement in a flow-through detector.

FIA is based on the injection of a liquid sample into a moving non-segmented continuous carrier stream of suitable liquid. As the sample is carried to the detectors, the fluid dynamics of flow through narrow bore tubing mixes the sample and reagent, when the detectable sample reach the flow-through cell the species is sensed by the detector which , most frequently photometric (Peat et al., 1997) although amperometric (Matos et al., 1998) , ion selective electrode (Alexander et al., 1997) , atomic absorption spectrometry (Feel et al., 1993), inductive coupled plasma (Nickson et al., 1999) , spectrometry (Sanches et al., 2000), Chemiluminescence (Barnett et al., 2000) and a number of others have also enjoyed much attention.

Very recently we construct a flow injection–electrochemical cell constructed with a single electrode for determination of $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple (Sulaiman and Al-Tae, 2002).

In this work a simple FIA instrument was designed, constructed and used in conjunction with multi-electrodes electrochemical flow-through cell containing the three working electrodes is applied to $\text{Cu}^{1+}/\text{Cu}^{2+}$ system.

EXPERIMENTAL WORK

Apparatus:

A typical FIA manifold is comprised of a pump, injection system, detection and tubing manifold.

Pump System:

The pump is used to propel one or more streams through the detection via narrow bore (0.3-0.8 mm internal diameter) tubing. The fluid is driven either by LKB peristaltic pump, or by gravity.

Injection Sample:

The sample was inserted or injected into a carrier solution by means of syringe-loaded injection.

Detection System:

A house-built multi-electrodes cell has been constructed for flow-injection electrochemical analysis (Fig.1). The detection system constructed in two parts, the auxiliary electrode (1 mm diameter Pt wire) and the working electrodes (GR, GC and PPPE) were placed in one part and the reference electrode (Ag/AgCl sat. KCl) placed in the second part connected to the cell solution by a vycor ceramic frit.

The three working electrodes positioned a part of (6 mm) from the auxiliary electrode. All electrodes were fitted into a teflon body cell as it is a good isolator and easy to machine. 1 mm diameter inlet and outlet drilled into the body cell. The two parts of the cell were clamped together with three screws. That designed permit readily change

the working electrodes from GC, GR or PPPE without taking the cell a part and also provide an easy access to the working electrodes in order to clean or polish the surface.

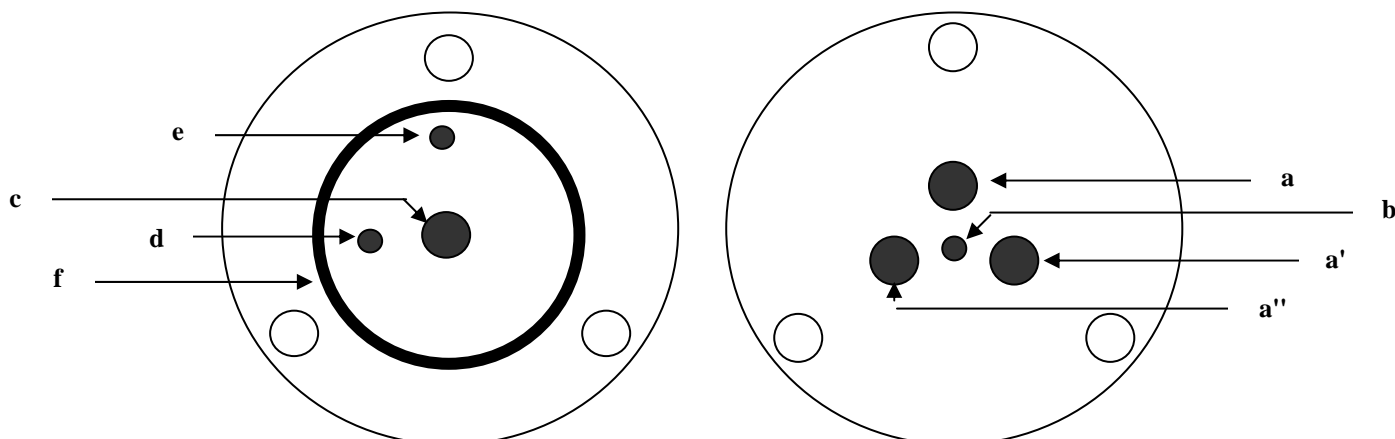


Fig. 1: Detector Configuration Internal-face view: a, a', a'' , working electrodes (5 mm diameter GC, GR and PPPE respectively); b, Auxiliary electrode (1.0 mm diameter Pt wire); c, Reference electrode (Ag/AgCl, Sat. KCl); d, inlet; e, outlet; f, o-ring washer.

Electropolymerization of Pyrrole Film:

The film was prepared either by static or flow mode using deaerated solution of 0.01 M pyrrole monomer in 0.1 M lithium perchlorate and holding the potential at +0.85V vs. Ag/AgCl sat. KCl for 10 min. in order to complete the coverage of GR or GC surface and formation of homogenous poly pyrrole film.

Notice:

All d.c voltammetric measurements were performed using a potentiostat type LB 75 and potentiometer SMP 72 supplied by Gerhard Bank Electronic for supplying the required potential, peak current was recorded using an x-t Fisher recordall series 5000. The cyclic voltammetric experiments were carried out using a potentiostat LB 75 and wave form generator type RB-2 supplied by CE chemical electronics (BIRTLEY) LTD. and the voltammograms were recorded using an x-y recorder BD 90 supplied by KIPP and ZONEN.

RESULTS AND DISCUSSION

Select of Applied Potential (E_{appli.}):

Two methods were employed to select the required potential for electrometric measurements, the first method represented by the cyclic voltammetry, scanning the potential between (0.1 to -0.3)V using GR or GC electrodes, whereas the second method, by employing different potentials from (+0.05 V) down to (-0.25 V) with increasing intervals of (0.05) and the response was recorded using an x-t recorder. The required potential for Cu¹⁺/Cu²⁺ couple was found to be (-0.1 V) on PPPE and ≈ (-0.2 V) on both GR and GC electrodes.

Effect of Flow-Rate:

The dependence of signal on flow-rate was studied (Sulaiman and Al-Tae), all parameters except the flow-rate were kept constant. The results show that the flow-rate (2.5-4.0) ml/min represent the optimum choice for measurement, this because the flow-rate is almost constant in this range, therefore, a small change in setting the flow-rate does not make a large change in peak current and this minimize the measurement error.

Effect of Concentration on Peak Current:

The relation between concentrations and peak current were examined for different concentrations of CuCl, CuCl₂ and mixture of them in (0.1 M) KCl which is act as supporting and carrier solution. A linear relations were observed at low concentrations whereas, a deviation seen at high concentrations.

For Cu¹⁺ (Fig. 2), this relation was linear in the concentrations range (0.08 – 2.0) × 10⁻³ M for oxidation process (I_{pa}) with r = 0.9922, S.D = 0.19, whereas for the reduction process the plot of I_{pc} versus concentration shows two lines, one at low concentrations in the range (0.08-1.0) × 10⁻³ M with r = 0.9871, S.D = 0.09 and second at high concentrations in the range (1.0-10.0) × 10⁻³ M with r = 0.9897, S.D = 0.20. The limit of detection for the two processes was 8.0 × 10⁻⁵ M.

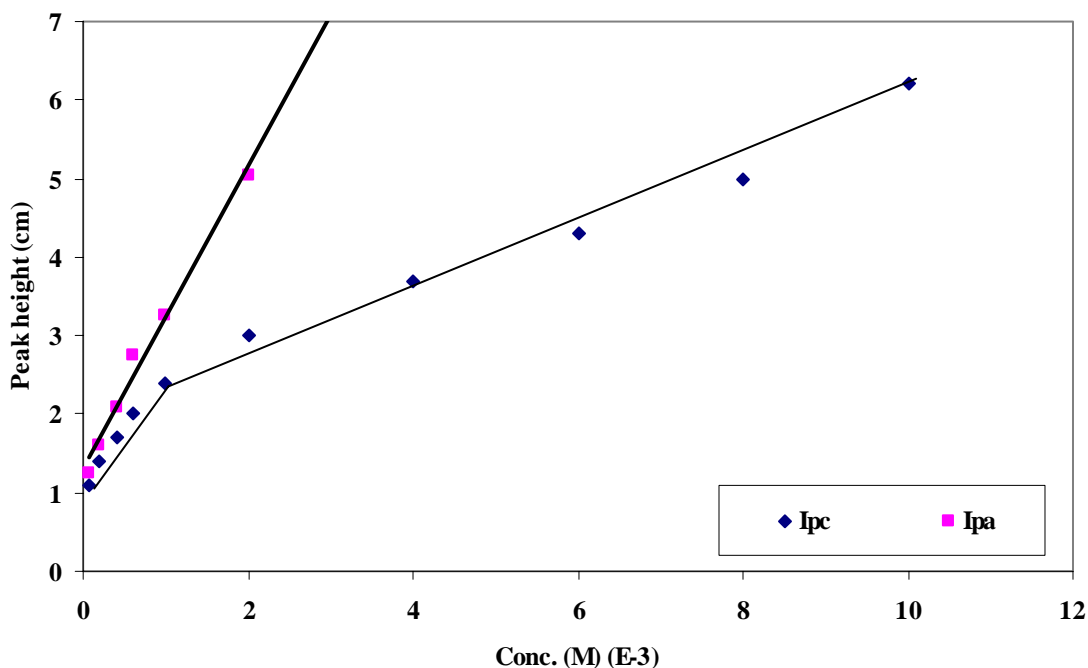


Fig. 2: Calibration curve of CuCl on GR electrode.

For Cu²⁺ on GR, the plot of I_p versus concentration, (Fig.3), shows two calibration curves for reduction process (conc. vs. I_{pc}), one at low concentration in the range (0.08-4.0) × 10⁻³ M with r = 0.9924, S.D = 0.1 and second at high concentration in the range (4.0-8.0) × 10⁻³ M with r = 0.9998, S.D = 0.04. On the other hand for oxidation process (conc. vs. I_{pa}) gives two calibration curves also, one at low concentration in the range (0.08-3.5) × 10⁻³ M with r = 0.9822, S.D = 0.3, and second at high concentrations in the

range $(3.5 - 8.0) \times 10^{-3}$ M with $r = 0.9998$, S.D = 0.05 The detection limit for the two process was found to be 8.0×10^{-5} M.

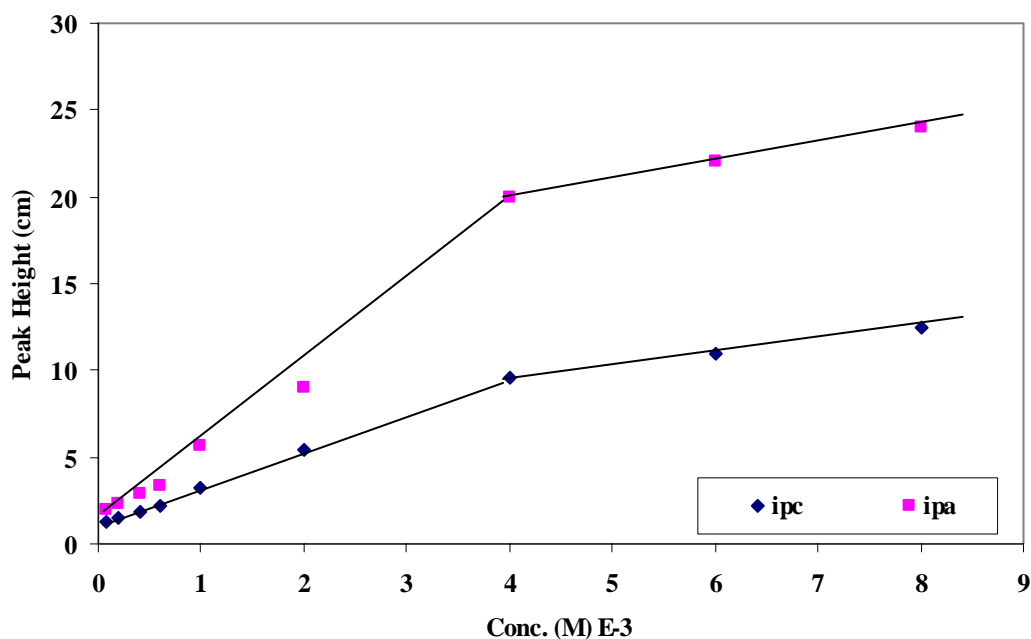


Fig. 3: Effect of Concentration on Peak height of CuCl_2 using GR electrode.

The plot of I_{p_a} versus concentration for Cu^{1+} on GC, (Fig. 4), gives a straight line with $r = 0.9878$, S.D = 0.45. On the other hand, the plot of I_{p_c} versus concentration gives two lines, one at low concentration in the range $(0.01-1.0) \times 10^{-3}$ M with $r = 0.9869$, S.D = 0.12 and second at high concentration in the range $(1.0 - 4.0) \times 10^{-3}$ M with $r = 0.9631$, S.D = 0.13. The detection limits for redox process was found to be 1.0×10^{-5} M .

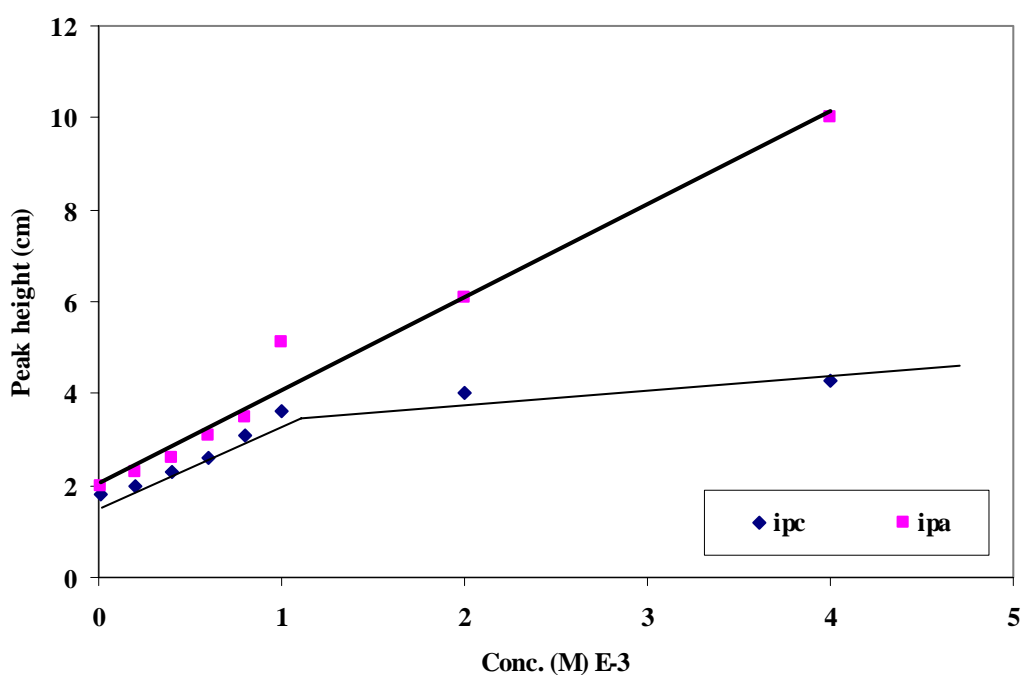


Fig.4: Effect of Concentration on Peak height of CuCl using GC electrode.

The plot of I_p versus concentration of $\text{Cu}^{1+}/\text{Cu}^{2+}$ in mixture on GC, (Fig. 5), gives a straight line for oxidation process (conc. vs. I_{pa}) in the range $(0.01-0.4) \times 10^{-3}$ M with $r = 0.9902$, S.D = 0.08, whereas for reduction process (conc. vs. I_{pc}) gives a straight line at low concentrations in the range $(0.01-0.4) \times 10^{-3}$ M with $r = 0.9927$, S.D = 0.05 and a deviation at high concentrations was observed. The limit of detection for both processes was found to be 1.0×10^{-5} M.

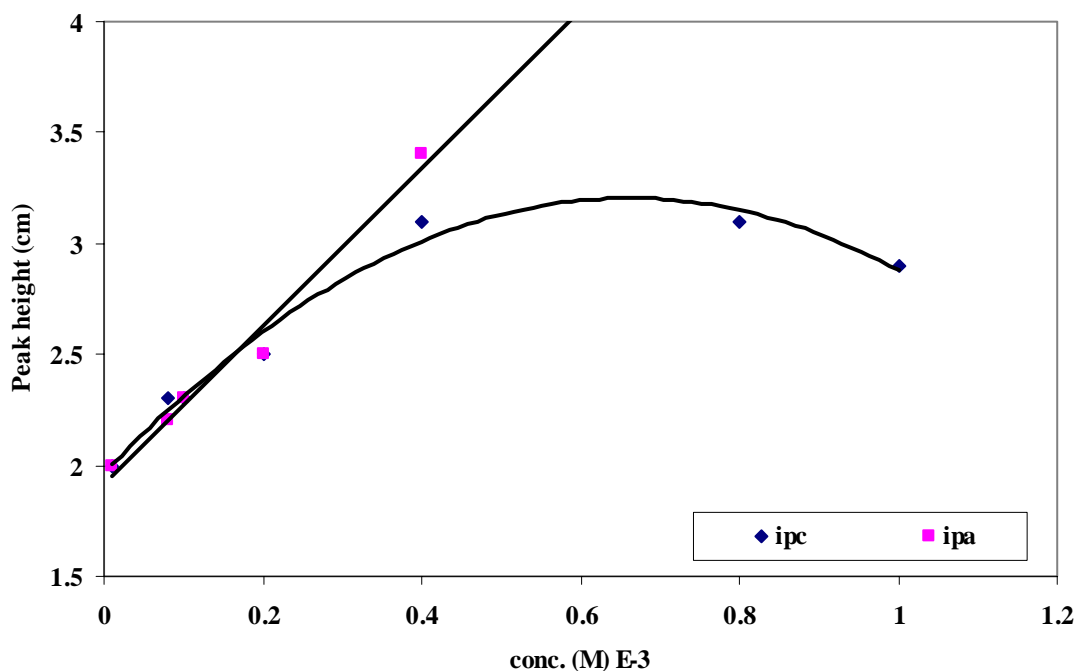


Fig. 5: Effect of Concentration on Peak height of CuCl and CuCl_2 mixture using GC electrode.

Effect of Cell Design:

To examine the causes of deviation at high concentrations, an experiment carried out using wall-jet mode, different concentrations of $\text{Cu}^{1+}/\text{Cu}^{2+}$ mixture in (0.1 M) KCl [with few drops of concentrated H_2SO_4 to dissolve CuCl], d.c voltammetry ($E_{\text{applied}} = -0.2\text{V}$) were used, the results shown in Fig (6), a linear relationship was obtained with $r = 0.9969$ and S.D = 0.28 for all the range of concentrations.

Calibration Curve of Cu^{2+} on PPPE:

Calibration curve of CuCl_2 was tested using PPPE and wall-jet-mode, $E_{\text{applied}} = -0.1$ V, 0.1 M KCl as supporting and carrier solution. The results shows that the plot of peak height versus concentration gives a linear relationship with correlation coefficient ($r = 0.9972$) and S.D = 0.02. The detection limit was found to be 1.0×10^{-7} M (6.3 ppb as Cu^{2+} ion).

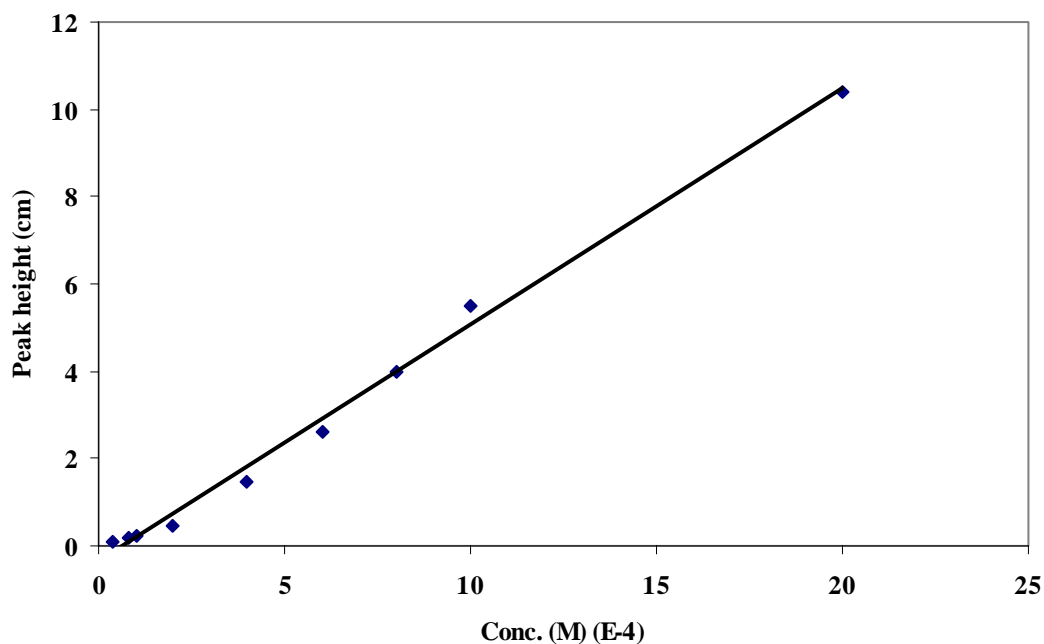


Fig. 6: Effect of cell design, using a mixture of CuCl and CuCl_2 , wall-jet mode (GR electrode) of operation.

CONCLUSION

Electrochemical detectors in combination with FIA can be used for the construction of inexpensive, rapid and simple instrumentations. Carbon in its various form, has found wide spread application in continuous flow detection, compared with other materials, carbon electrodes are characterized by a large anodic and a moderately large cathodic potential range at the same time they displayed high stability and low residual currents.

During this work it has been demonstrated that the wall-jet cell design is well suited as multi-electrodes detector in electroanalytical flow based measurements, because that design has three great advantages, first, there are no rotating parts; the solution can be impelled through the jet by a pump or by gravity feed; secondly, there is a very small effective dead volume; thirdly, the wall-jet design yields fast response and high sensitivity. PPPE gives the best results with the lowest detection limit.

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