

Testing of Electrochemical Efficiency of Wall-Jet Cell FC2 as a Tool for Detection of Electrochemically Oxidisable Biomarkers

Jan Krejčí¹, Iva Ventrubová¹, Lucie Ježová¹, Jan Fischer², Jiří Barek^{2,*#}

¹ BVT Technologies, a.s., Hudcova 78c, 612 00 Brno, Czech Republic

² Charles University in Prague, Faculty of Science, University Research Centre UNCE "Supramolecular Chemistry", Department of Analytical Chemistry, UNESCO Laboratory of Environmental Electrochemistry, Albertov 6, CZ-128 43 Prague 2, Czech Republic, e-mail:

*E-mail: Barek@natur.cuni.cz

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In order to test the suitability of newly developed wall-jet electrochemical cells FC2 for detection of electrochemically active biomarkers, electrochemical efficiency of those cells have been characterized using $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple as a probe. Measurements were performed in the range of Reynolds numbers from 0.067 to 21.3 for flow rates 0.1 – 32 ml/hr. Efficiency of the cells were found to be in the range of 0.06 – 5.3 %. The dependence of efficiency E on the flow rate Q follows the equation $E(\%) = a \times Q^b$ ($a = 0.855$, $b = -0.746$; $[Q] = \text{ml/hr}$) with $R = 0,999$. The difference between the three cells can be characterized by SD of a and b (8.2 % and 5.2 %, respectively). The dependence of current I (nA) on the flow rate Q follows the same equation $I(\text{nA}) = a \cdot Q^b$ with $a = 2294$ and $b = 0,255$ (SD = 8.2 % and 14.7 % for a and b, respectively). FC2 cell with wall-jet hydrodynamics provides reproducible electrochemical measurements with well-defined efficiency and current flow dependence.

Keywords: Wall-Jet detector, electrochemical cell, efficiency, flow analysis.

1. INTRODUCTION

There is an ever increasing demand for inexpensive, fast, reliable and simple analytical methods suitable for large scale monitoring of tumor biomarkers in urine, examples of them being easily electrochemically oxidisable vanylmandelic acid and 4-hydroxy-3-methoxymandelic acid. Electrochemical measurements in flowing systems with wall-jet electrochemical detector are one of

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possible solutions of this problem. Matsuda and Yamada J. [1, 2] first defined and characterized flow cell with wall-jet arrangement (WJ). Many applications of WJ were published since first publication appeared. Lexa (1994) used WJ arrangement in potentiometric measurement of Cl^- [3]. Comparison of WJ with RDE (rotated disk electrode) was made by Lindgren in the study of direct electron transfer kinetics of HRP (horse radish peroxidase) [4]. WJ arrangement was used for lead detection in blood [5]. Comprehensive analysis of flow electroanalytical method including WJ was made by Štulík [6]. Kurita described WJ cell with interdigitated electrodes [7]. Bart used the electrochemical WJ detection in combination with surface plasmon resonance [8].

An important parameter of the flow cell is the current efficiency. It specifies the ratio between current, which is measured and current, which would arise if all substances entering the cell is electrochemically converted. The knowledge of WJ cell efficiency and current flow dependency simplifies the experimental design [9]. The reproducibility between cells is an important parameter which enables their practical use. Therefore, detailed specification of these parameters for FC2 cells is the aim of this work.

2. EXPERIMENTAL

The wall-jet cell FC2 (BVT Technologies, www.bvt.cz, Brno, CZ) was connected directly to a linear pump Technic I (AMV, www.amvtechnics.cz, Brno, CZ) using plastic capillaries of internal diameter (ID) 0.3mm. The sensor (AC1.W2.R1 (BVT Technologies, www.bvt.cz, Brno, CZ) with platinum working electrode and a reference Ag/AgCl electrode) was inserted into the cell and locked. The cell construction was optimized to prevent accumulation of air bubbles. The cell was connected to PC using the USB Bioanalyzer potentiostat (BVT Technologies, www.bvt.cz, Brno, CZ). The solution containing of 10 mM $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple in 0.04M NaOH as a probe and sensor AC1.W2.R1 (BVT Technologies, www.bvt.cz, Brno, CZ) with platinum working electrode and Ag/AgCl (3M KCl) reference electrode were used. Applied potential was + 650 mV vs Ag/AgCl reference electrode Data were recorded using the software of Bioanalyzer potentiostat and analyzed by means of the Excel software (Microsoft).

3. RESULTS AND DISCUSSION

3.1. Characterization of the flow

Reynolds number Re was calculated by using the hydraulic diameter of the tube d , the mean flow velocity in the cross section v_s and kinematic viscosity ν :

$$Re = v_s \cdot d/\nu$$

Reynolds number ranged from 0.067 to 21.3 for flow rates from 0.1 – 32 ml/hr. These values prove that the measurement was done in laminar flow mode.

3.2. Principle of the flow cell measurement

Schematic chart of the cell with dimensions is in Figure 1.A. The photography of the cell is in Figure 1B. The cell is designed for the standard screen printed electrodes AC1 or CC1 (BVT Technologies, www.bvt.cz, Brno, CZ). It enables simple exchange of the electrodes and their effective use.

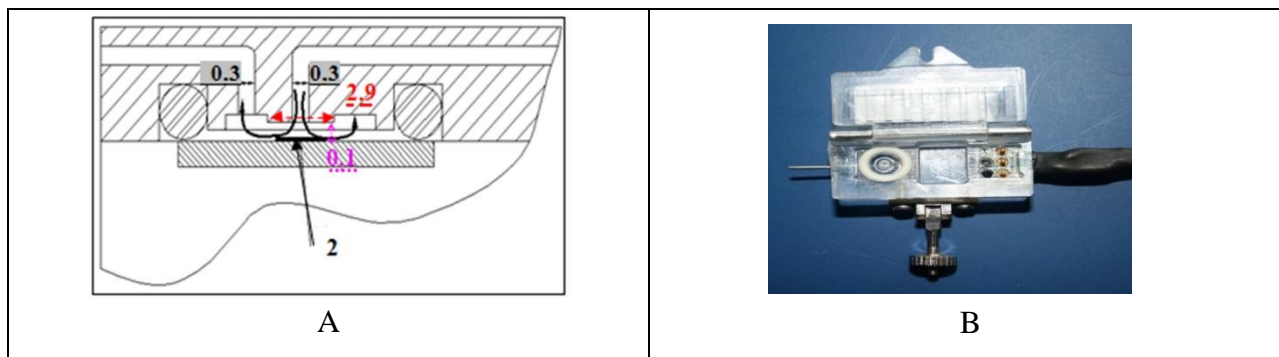


Figure 1. A: Arrangement of wall jet flow cell FC2. (Cell dimensions are given in millimetres.) B: FC2 wall jet photograph.

The dependence of current on the flow rate follows equation $I(\text{nA}) = a \cdot Q^b$ with $a = 2294$ and $b = 0.255$ (standard deviation is 8.2 % and 14,7 % for a and b , respectively). Average values of three cell currents are shown in the Figure 2. The values a and b are in agreement with data published by Kurita [7].

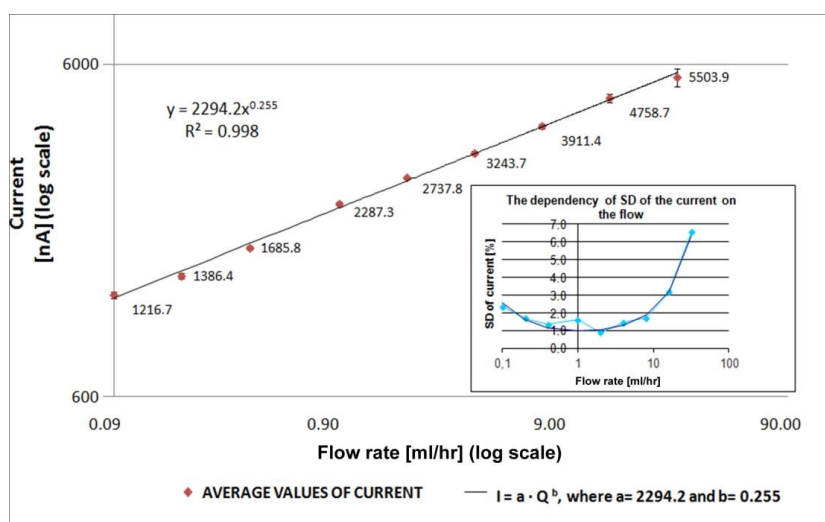


Figure 2. Dependency of cell current on flow rate (log-log scale axis).The dependence of SD of current on the flow rate is in inset.

3.3. Reproducibility

The stability and precision of the flow rate is the key factor for measurement reproducibility. Therefore, the stability of the flow rate generated by the linear pump Technic I (AMV, www.amvtechnics.cz, Brno, CZ) was further investigated.

3.4. Properties and stability of the pump flow

Stability of flow of the linear pump AMV Technic I depends on the chosen syringe. Real flow rates of the used pump are shown in Figure 3.

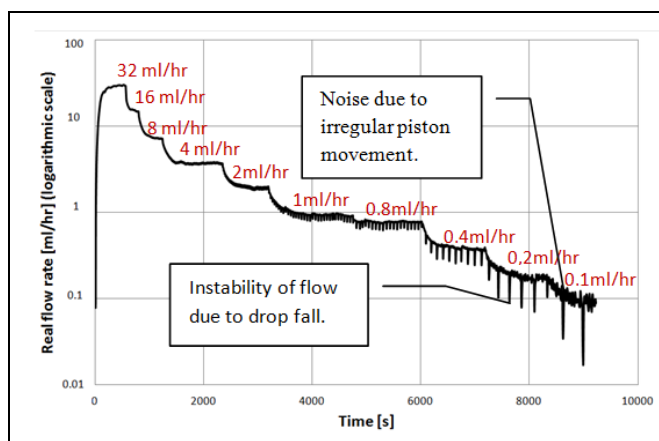


Figure 3. Dependence of real flow rate generated by linear pump AVM Technic I in semilog scale.

The used linear pump AMV Technic I assures good flow rate stability after 100 s of stabilization (see Figure 4). At extremely low flow rates the flow rate is influenced by piston movement and by instability caused by the drops of liquid which falls-off at the end of output tubing (see Figure 3).

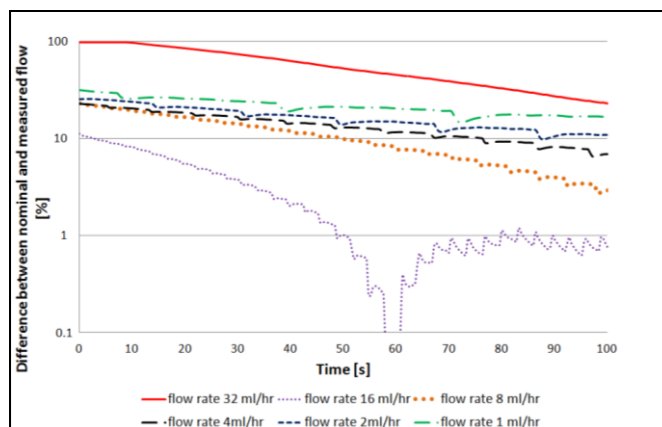


Figure 4. Stabilization of the flow rate generated by linear pump AVM Technic I when it is decreased to a half.

3.5. Efficiency

The maximum current which can be generated on WJ electrode arrangement can be determined by means of the charge corresponding to the total number of exchanged calculated from the input mass flow of the tested electroactive compound. Experimentally it was determined as the product of the input flow rate into the cell Q , concentration of the substance c and Faraday constant F ($F = 9.6485 \cdot 10^4 \text{ C/mol}$).

$$I_0 = Q \cdot c \cdot F$$

The efficiency of the cell was then determined by calculating the ratio of the measured current I to the current I_0 corresponding to full conversion.

$$\eta = I/I_0$$

Capillary of the used WJ detector has a diameter 0.3 mm. The efficiency decreases with the increased flow which can be explained by a lower contact time of electroactive substance with electrode surface. For higher flow rates the contact time is so low that the majority of electro active compound's molecules cannot exchange electrons with the electrode (seed Figure 5).

Efficiency of the cells are in the range of 0.06 – 5.3%, i.e. far from the coulometric regime. The dependence of efficiency η on the flow rate Q follows the equation $\eta = a \cdot Q^b$ ($a = 0.8547$, $b = -0.746$ [Q] = ml/hr) with $R = 0.999$. The difference between three tested cells can be characterized by means of SD of a and b (8.2 % and 5.2 %, respectively).

It is interesting to note that both SD of current and SD of efficiency decreases with flow rate. It suggests quite plausible explanation that electrode behavior is fairly reproducible and that the main source of variability is hydrodynamics, i.e. transport of electroactive molecules to the electrode surface.

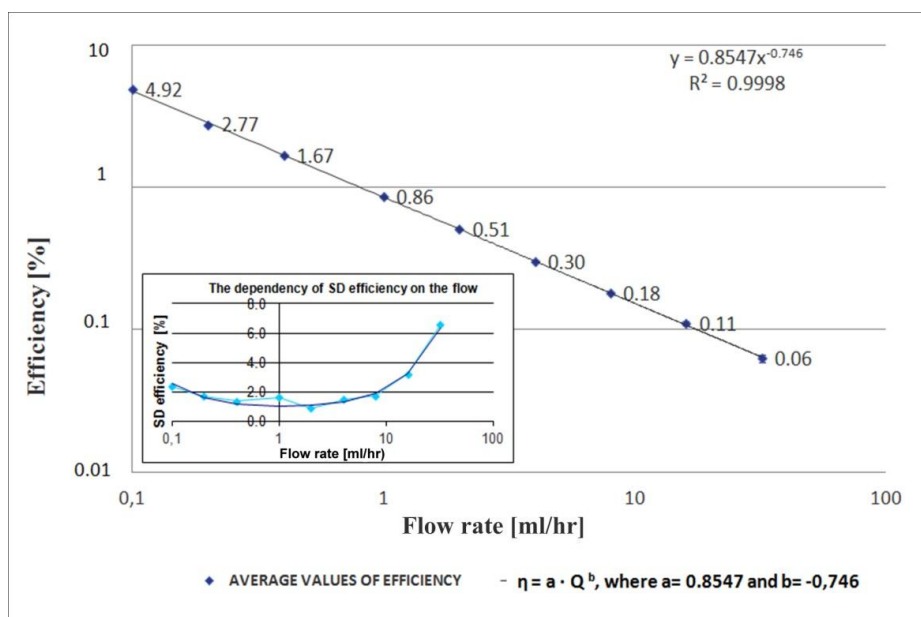


Figure 5. The dependence of the efficiency of electrochemical conversion on the flow rate (log-log scale).

4. CONCLUSION

It has been proven that electrochemical cells FC2 with WJ arrangement provide well reproducible results and thus they are a suitable tool for monitoring of electrochemically oxidisable biomarkers. The cell is small, robust and it enables to use screen printed electrodes AC1 for classical electrochemical measurement or CC1 electrodes with interdigitated structures (BVT Technologies, www.bvt.cz, Brno, CZ). The cell FC2 has sufficient reproducibility and stability which enables its application for determination of micromolar concentrations of electrochemically oxidisable compounds. Moreover, if a well-studied electrochemical system is used as a probe, it can be used as a highly precise flowmeter to measure extremely small flow rates. The dependency of current of the flow rate can be described by equation:

$$I = 2294 \cdot Q^{0,255}$$

The knowledge of the parameters of this dependency enables to carry out the measurement of diffusion coefficients and the detailed kinetic studies.

The dependency of efficiency on the flow rate which follows equation $\eta = 0.8547 Q^{-0.746}$ enables to optimize simply the experiment with respect to the used flow rate and analyte concentrations.

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References

1. H. Matsuda, *J. Electroanal. Chem.* 15 (1967) 109.
2. J. Yamada, H. Matsuda, *J. Electroanal. Chem.* 44 (1973) 189.
3. J. Lexa, K. Stulik, *Talanta* 41 (1994) 301.
4. A. Lindgren, F. D. Munteanu, I. Gazarya, T. Ruzgas, L. Gorton, *J. Electroanal. Chem.* 458 (1998) 113.
5. S. Jaenicke, R. M. Sabarathinam, B. Fleet, H. Gunasingham, *Talanta* 45 (1998) 703.
6. K. Štulík, V. Pacáková, *Elektroanalytická měření v proudících kapalinách*, SNTL - Nakladatelství technické literatury, Praha (1989), p. 305.
7. R. Kurita, H. Tabei, Z. Liu, T. Horiuchi, O. Niwa, *Sensor. Actuat. B-Chem.* 71 (2000) 82.
8. M. Bart, P. J. H. J. van Os, B. Kamp, A. Bult, W. P. van Bennekom, *Sensor. Actuat. B-Chem.* 84 (2002) 129.
9. R. Sejnohova, V. Hanak, J. Krejci.: *Screen printed electrodes improve mass transfer*. In: New perspectives in biosensors technology and applications (P. A. Serra, Ed.), InTech, Rijeka, Croatia (2011).