Chinese Chemical Letters Vol. 16, No. 12, pp 1629-1632, 2005
http://www.imm.ac.cn/journal/ccl.html

The Determination of Iodide Based on a Flow-injection Coupling Irreversible Biamperometry

Li Jun LI[1]*, Hao CHENG[2], Wen Yi HUANG[2], Hong Xing KONG[1],
Jian Ling WU[2], Jian Ping LU[2], Wei GAO[3], Jun Feng SONG[3]

[1]Department of Biological and Chemical Engineering,Guangxi University of Technology,
Liuzhou 545006
[2]College of Chemistry and Chemical Engineering,Guangxi University, Nanning 530004
[3]Institute of Analytical Science, Northwest University, Xi'an 710069

Abstract: A novel flow-injection irreversible biamperometric method is described for the direct determination of iodide. The method is based on electrochemical oxidation of iodide at the gold electrode and the reduction of permanganate at the platinum electrode to form an irreversible biamperometric detection system. Under the applied potential difference of 0 V, in the 0.05 mol/L sulfuric acid, iodide can be determined over the range 4.00×10^{-7}-1.00×10^{-5} mol/L with a sampling frequency of 120 samples per hour. The detection limit for I^- is 3.0×10^{-7} mol/L and the RSD for 40 replicate determinations of 4.0×10^{-5} mol/L potassium iodide is 1.68%. The new method was applied to the analysis of iodide in table salt with satisfactory results.

Keywords: Iodide, flow injection, irreversible biamperometry, gold electrode, platinum electrode.

As has been shown[1-3], biamperometric detector with two electrodes polarized with a small potential difference is useful in flow injection analysis. Based on the principle of dead-stop end point detection, the method shows high sensitivity and high selectivity. Unfortunately, only few reversible couples like I_2 / I^-, Br_2 / Br^- have been successfully used for analytical purpose so far. The biamperometry used for irreversible system has been briefly introduced[4,5]. In the scheme, the biamperometric detection was established by coupling two independent and irreversible electrode couples their electrode processes were inverse and half-wave potentials were close to each other as possible. The method allows direct determination of analytes undergoing irreversible electrode process with a very small applied potential difference, even 0 V. Since the applied ΔE was very small, the method showed high selectivity and signal to noise (S/N) ratio. It has been successfully applied to the determination of vitamin C, hydroxylamine, cysteine[6], *etc*. Through the review on the application of gold, platinum, glass-carbon electrode in reversible biamperometry, Sacchetto G. A. pointed out that the gold electrodes can also be applied to biamperometry[7], moreover it has even smaller background current and satisfactory sensitivity. Gold was found to be the most suitable material in the biamperometry detector. But there is little report on the study of gold electrodes used in

---

[*] E-mail: lilijun0562@sina.com

biamperometry.

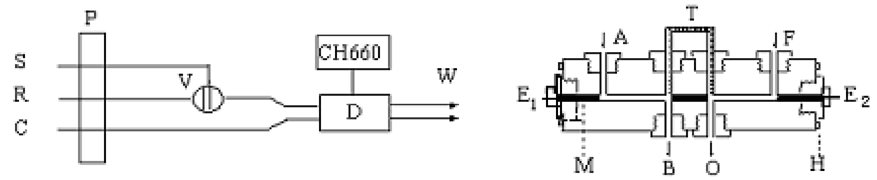
As iodide was found to be oxidized on the gold electrode at much high positive potential, in this work, the reduction potential of permanganate on the platinum electrode near to oxidation potential of iodide on the gold electrode. The biamperometry detection scheme was established by coupling the oxidized of iodide with an irreversible reduction of permanganate. With the advantages of the applied ΔE of 0 V, and addition of any other reaction reagent is not necessary, satisfactory sensitivity, selectivity and high S/N, the proposed method was suitable for automatic and continuous analysis of iodide.

Experimental

A CHI660 Electrochemical Workstation (CH Instrument, USA) was used to perform the cyclic voltammetric experiments. The cyclic voltammograms were obtained with a three-electrode system, namely a platinum wire or a gold wire working electrode, a platinum auxiliary electrode and a saturated calomel electrode (SCE).

A flow injection system was included an automatic sampling system (IFIS-B, Ruike Electronic Instrument Limited Co., China), which was equipped with two peristaltic pumps and a six-way injection valve, controlled by a microcomputer. The schematic diagram of the homemade biamperometric detector, which was constructed from a Teflon rod. The assembly of the detector was illustrated in **Figure 1**. A potential difference (*ΔE*) of 0 V was kept across the two wire electrodes and the cell current was recorded by the CH660 workstation. Calibration graphs were obtained by plotting the current versus standard concentration of iodide, and the content of each sample was determined.

Figure 1 Schematic diagram of the flow injection system

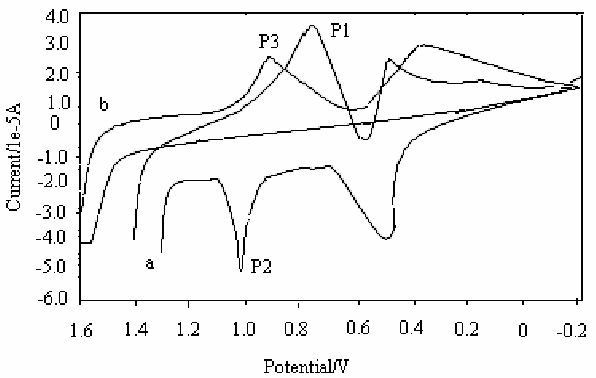


P: Peristaltic pump; V: 6-channel valve; S: Sample; R: Carrier solution; C: Counter solution; D: Detector; W: Waste; A: Sample inlet; B: Sample outlet; E_1: Gold wire electrode; E_2: Platinum wire electrode; F: Counter solution inlet; O: Counter solution outlet; M: Epoxy sealant; T: Salt bridge; H: Holes for machine bolts.

Results and Discussion

Figure 2 showed that the oxidation wave P_2 and the reduction wave P_3 were separately in anodic and cathodic polarized curves, they were from two independent and irreversible couples with the potential difference of only 0.16 V. According to the irreversible biamperometry, the biamperometric detection scheme was established by coupling the oxidation of potassium iodide with the reduction of permanganate. In this case, the determination can be carried out with a small applied *ΔE* even 0 V. Moreover, the two reactants were separated into two electrode rooms by means of a salt bridge when perfor-

Figure 2 Cyclic voltammograms of the potassium iodide/permanganate biamperometric system



a: The oxidation of 10^{-3} mol/L potassium iodide; b: The reduction of 10^{-3} mol/L permanganate; Scan rate: υ = 100 mV/s; Initial potential: -0.2V; Reversal potential: 1.5V.

ming the flow injection determination, which avoids the influences from the homogeneous reaction of I^- and MnO_4^-.

The experiments indicated that the maximal S/N ratio was obtained with the applied ΔE of 0 V. Thus, the applied ΔE of 0 V was chosen in this work. As a tradeoff, in present work, 0.5 mol/L of H_2SO_4 solution was selected as the carrier solution and concentration of the potassium permanganate was 1.0×10^{-3} mol/L.

Such parameters of the FIA operation as flow rate, injection volume and others were optimized by using 4.0×10^{-4} mol/L potassium iodide standard solution. In consideration of some factors, the injection volume and the flow rate were chosen as 100 μL and 2.8 mL/ min, respectively. The distance between the detector and the valve had no obvious effect on current response and the distance was 24 cm.

The tolerance limit of additives to 4.0×10^{-5} mol/L potassium iodide were ≥200-fold of Mg^{2+}, K^+, Ba^{2+},Al^{3+}, 25-fold of Ca^{2+} CO_3^{2-}、PO_4^{3-}、Cl^-、NO_3^- ,Fe^{3+}, Cu^{2+},respectively.

Under the optimized conditions, the biamperometric detector had good response to potassium iodide standard solutions. The linear relationship between the cell current and the concentration of potassium iodide in the range of 4.0×10^{-7} to 1.0×10^{-5} mol/L was obtained. The linear regression equation was Y=0.00431X+4.01202E-9 with a regression coefficient r = 0.9987 (n = 9). The detection limit (LOD) for S/N=3 was 3.0×10^{-7} mol/L. The precision of the method shown by RSD of 1.68% for 40 replicate determinations of 4.0×10^{-5} mol/L potassium iodide was good.

Table 1 Analytical results of samples

Sample	Concentration (10^{-6}mol/L)	RSD(n=5) (%)	Added (10^{-6}mol/L)	Found (10^{-6} mol/L)	Recovery (%)	Average (%)	RSD (%)
1	1.80		4.00	5.77	99.2		
2	1.68		4.00	5.68	100		
3	1.74	1.8	4.00	5.60	96.5	98.4	1.34
4	1.76		4.00	5.68	98.0		
5	1.76		4.00	5.70	98.5		

Exactly weigh 10.0 g package salt solid in district, dissolve it with 0.05 mol/L H_2SO_4, diluted and fixed its volume to 100 mL, then measured it for 5 times. The recoveries obtained are listed in **Table 1**.

Acknowledgment

Thanks for the financial support of the Guangxi Science Fund For Youth (No. 0135003) and Guangxi Universities One Hundred Young–middle Scholar Fund for the present work.

References

1. M. Trojanowicz, A Hulanicki, W Matuszewski, *Anal. Chim. Acta*, **1986**, *188*, 165.
2. J. Kurzawa, *Anal. Chim. Acta*, **1985**, *173*, 343.
3. P. Karabinas, D. Jannakoudakis, *J.Electroanal.Chem.***,** **1984**, *160*, 159.
4. J. F. Song, C. Zhao, X. F. Kang, *et al*., *Chem. J. Chin. Univ,*, **2000**, *21*(4), 535.
5. J. F. Song, C. Zhao, W. Guo, *et al*., *Anal. Chim. Acta*, **2002**, *470*, 229.
6. J. Q. Chen, J. F. Song, *Chinese Journal of Analysis Laboratory，Supplement*，**2003**, *22*, 353.
7. G. A. Sacchetto, P. Pastore, G. Favaro, *et al*., *Anal. Chim. Acta*, **1992**, *258*, 99.

Received 26 May, 2005