Biamperometry in the Diffusion Current Region: Considerations For Its Application In Trace Analysis

Jaim Lichtig*, Dimas Augusto Morozin Zaia, José Pedro Serra Valente

and Maria Olimpia de Oliveira Rezende

Instituto de Química - USP, Caixa Postal 20780
01498 São Paulo, SP, Brasil

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Reestudou-se a biamperometria, constantado-se ser possível o uso da mesma em análise de traços. Dois sistemas reversíveis foram estudados: I_2/I^- e Br_2/Br^-. Vários parâmetros foram estudados, como: área dos eletrodos, diferença de potencial aplicado entre os eletrodos e relação molar dos componentes do par reversível em solução. Os estudos mostraram que o processo de difusão fundamental no fenômeno, quando se consegue retas através de gráficos corrente vs. concentração da espécie. A geração de I_2 e Br_2 efetuada *in situ* pela adição de soluções padrões de IO_3^- e BrO_3^-, a soluções contendo excesso de I^- e Br^-, respectivamente, em meio ácido. No caso de I_2/I^-, uma diferença de potencial de 100 mV usada e, no caso de Br_2/Br^-, 300 mV, com relações molares, respectivamente: $I_2/I^- \geq 50$ e $Br_2/Br^- \geq 1500$. Nessas condições o método biamperométrico pode ser usado de duas maneiras: pela titulação ou pela adição de solução padrão. Determinações de 10 ppb de espécies poluentes podem ser efetuadas com boa precisão e exatidão. O equipamento utilizado de baixo custo e torna a titulação microcoulométrica obsoleta.

The best conditions for obtaining straight-lines in biamperometric analysis were studied with the redox systems: I_2/I^- and Br_2/Br^-. Parameters such as voltage across the platinum electrodes, size of the electrodes and molar ratio of the components of each of the redox pairs in solution are very important and this study has shown a diffusion process at the electrodes. The generation of I_2 or Br_2 in solution is made by adding volumes of standard IO_3^- or BrO_3^- in solutions containing I^- or Br^-, respectively, in acid medium. When 100 mV and molar ratio $I^-/I_2 \geq 50$ in the case of I_2/I^- pair and 300 mV and molar ratio $Br^-/Br_2 \geq 1500$ are used, one can obtain straight lines on ploting current measured vs. added volume of IO_3^- or BrO_3^- respectively. In these conditions the method can be used in two ways: or titration or through standard addition and good accuracy is achieved in trace analysis, even 10 ppb determinations. The equipment is of low-cost and can make microcoulometric titrations to be obsolete.

Key words: *biamperometry; trace analysis; environmental analysis*

Introduction

As early as 1897, Salomon used two polarizable electrodes[1,2] for the argentometric determination of chloride. In 1905, Nernst and Merriam[3] used this technique for acidimetric determination and in 1926, Foulk and Bawden[4] did a more extensive study based on the measurement of the current developed between two identical electrodes at a constant applied voltage. They called this approach "dead-stop end-point method", because iodine is titrated with thiosulphate and the current comes to a sudden stop.

In subsequent years, this method found wide use in analytical chemistry, mainly in the determination of water using the Karl Fischer reagent[5,6]. From this point the method had few applications only perhaps due to the empiric way in which the technique was used without a rational electrochemical explanation. Only in 1950, Delahay[7] presented a more adequate explanation for the dead-stop titration interpreting potential vs. current curves. Later, in 1954, Kolthoff[8] renamed this technique "biamperometric titration" and Delahay further described it in his book[9]. His description is based on polarization curves of the titration systems which are schematically presented in Figure 1.

When two identical platinum electrodes are placed in the solution to be titrated, they attain the same potential and no current flows. If both oxidized and reduced forms of a

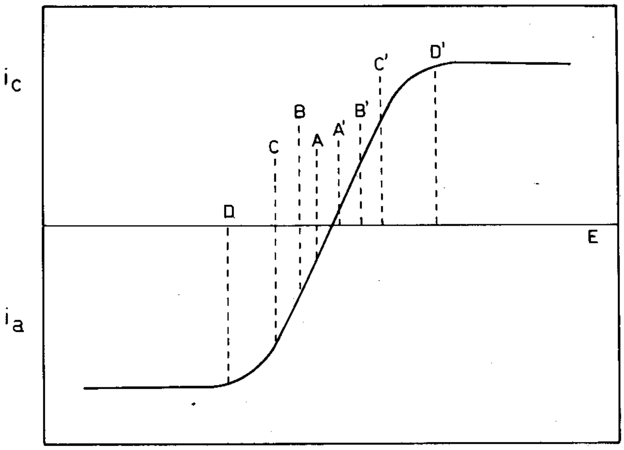

Figure 1. *Current versus voltage of a reversible system: I_3^- (I^-, with two platinum electrodes (1 cm^2 each) immersed in the solution. AA' = 10 mV; BB' = 30 mV; CC' = 60 mV; DD' = 100 mV*

reversible redox couple are present, a small applied potential to the two electrodes will cause a current to flow (AA' Figure 1). If both forms of an irreversible redox system are present, a current will flow only if the applied potential is greater than the sum of the anodic and cathodic overpotentials (Figure 2). In either case, considering a redox system in solution, the current results from the reduction of the oxidized form at the cathode and the oxidation of the reduced form at the anode. If only one form (either reduced or oxidized) of a redox system is present, no current flows. The consequence is that, during a biamperometric titration, maintaining an appropriate voltage between the electrodes, with the consumption of the oxidized or reduced form of a system, when both are present in solution, at the end-point the current is zero or almost close to it. A classical example is the biamperometric titration of I_2 (I_3^- / I^- system) with $S_2O_3^{2-}$(Figure 3).

Either before the end-point or beyond it, a current may or may not flow (with a small applied potential between the electrodes) depending on whether the titrant, or titrated system, or both are reversible. Therefore, if a current flows, it will change in the course of the titration process (which includes the addition of titrant in excess beyond the end-point) as the ratios of the concentrations of the oxidized to reduced forms of the components of the main redox system change. Virtually no current flows in irreversible systems because the applied potential, in most cases is not enough to develop a current.

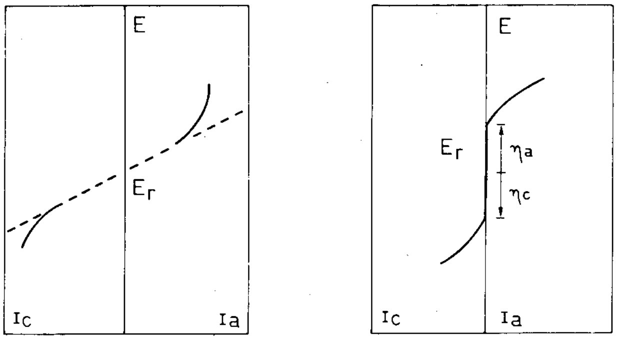

Figure 2. *Current versus voltage of a general system: reversible (left) and irreversible (right); η_a and η_c are the overpotentials of anode and catode respectively. Two platinum electrodes.*

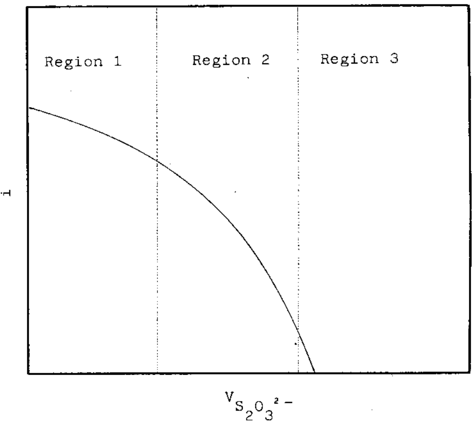

Figure 3. *Biamperometric titration of I_2 (I_3^-) in solution containing I^- with $S_2O_3^{2-}$; i = current. $V_{S_2O_3^{2-}}$ = volume of $S_2O_3^{2-}$ solution added; two platinum electrodes.*

The equations describing titration curves in biamperometric titration have been derived by various workers on the bases of the polarization curves of the titration systems[10-14]. From these authors it follows that both branches of the titration curves have a hyperbolic form and become linear in the vicinity of the end-point. For reversible, as well as irreversible redox system, charge transfer coefficients of $\alpha = 1$ and $\alpha = 0.5$ respectively, indicate that the titration curves up to the equivalent point are symmetrical hyperbolas with respect to the point at which half the volume needed to reach the equivalence point has been added. For example, when Fe(II) is titrated biamperometrically with Ce(IV), at the beginning of the titration no current flows because only Fe(II) is present in the solution. As Fe(III) is formed, during the course of the titration, the current increases because the ratio [Fe(III)]/[Fe(II)] increases. At the half-way titration point, when the concentration of Fe(II) and Fe(III) are equal, the current reaches a maximum. Beyond this point, the [Fe(II)]/[Fe(III)] governs the titration and the current decreases. At the end-point with the concentration of Fe(II) essentially zero, only the background current flows. Beyond this point, the current increases as a result of an increase in the concentration of Ce(IV), which forms a new reversible redox couple with Ce(III) (Figure 4).

According to this way of titration complexants, such as: mainly EDTA, were used to determine metals, Fe(III) [15], Ni[16], Co [17] and Bi [18].

Rationale for the Current Work. We emphasize that the parameters of biamperometry can be quite the same as those of polarography. So, if a fixed potential is applied between

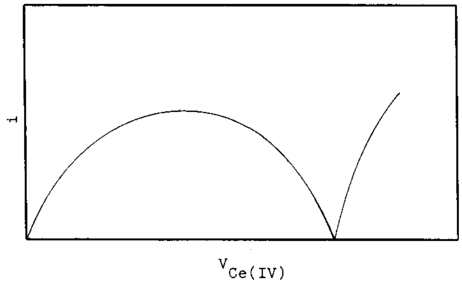

Figure 4. *Biamperometric titration of Fe(II) with Ce(IV) solution; i = current;* $V_{Ce(IV)}$ *= volume of Ce(IV) solution added; two platinum electrodes.*

two platinum electrodes immersed in a solution containing I_2 and I^- (actually I_3^- and I^-), a current flows, as mentioned. To interpret the phenomenon, on using the voltametric curves (Figure 1), which are similar to the polarographic ones, we can consider that the resulting current can be seen similar as that one obtained by polarography, that is, the current should be the result of a sum of migration current and diffusion current. If in the above mentioned solution there is an excess of I^-, or another ion, we can consider it as the supporting electrolyte and, therefore, the migration current to be practically constant. As a constant potential is applied between the two electrodes with constant area, we can consider the capacitive current to be zero. In these conditions, the current obtained should be only due to diffusion phenomenon.

We also consider the maintenance of the diffusion layer around the electrodes as fundamental for the best use of the biamperometry.

According to Bard[19] and later confirmed by Rabockai[20-22], the electrode configuration determines the maintenance or not of the diffusion layer around the electrode. Thus, if the configuration is not appropriate, the diffusion layer is not steady and can collapse. The small electrodes (Pt wire, small Pt foils, or Pt disk, for instance), can maintain the diffusion layer. A Pt gauze electrode does not maintain the diffusion layer. The eventual stirring of the solution forces a decrease in the thickness of the diffusion layer with the concomitant increase of the current measured.

One can understand the 3 regions in Figure 3, concerning the titration of a solution of I_2/I^- (actually I_3^-/I^-) with $S_2O_3^{2-}$.

If the system is reversible, the overpotential amount can be neglected when a small e.m.f. is applied between the two platinum electrodes. Consequently, in Figure 3, region 1, one has:

$$E = iR \qquad (1)$$

where E is the potential applied between the electrodes.

If we add a substance that reacts with I_2, thus reducing its concentration, the concentration overpotential at the platinum electrodes cannot be neglected (region 2 in Figure 3), and:

$$E - iR = E_a - E_c \qquad (2)$$

where E_a and E_c are the anode and cathode potentials, respectively.

In region 3, near the end point, iR is too small when compared to ($E_a - E_c$) and one can write:

$$E = E_a - E_c \qquad (3)$$

At the surface of the electrodes, the following equations apply:

$$I_2 + 2\,e^- \rightleftharpoons 2\,I^- \text{ (cathode)}$$

$$2\,I^- \rightleftharpoons I_2 + 2\,e^- \text{ (anode)}$$

Considering the system I_2/I^- as one electron transfer system, according the Nernst equation, one has:

$$E_a = K + (RT/F)\ln(c_a^o/c_I^-) \qquad (4)$$

$$E_c = K + (RT/F)\ln(c_c^o/c_I^-) \qquad (5)$$

where: c_a^o = concentration of iodine at anode electrode
c_c^o = concentration of iodine at cathode electrode
c_I^- = concentration of iodide in the solution

The resulting current can be related to the concentration:

$$i = k\,(c_a^o - c) = K\,(c - c_c^o) \qquad (6)$$

where c is the concentration of iodine in the bulk of the solution.

k is the same for both electrodes (same area) and for reversible systems. Consequently:

$$c_a^o + c_c^o = 2\,c \qquad (7)$$

From equations (3) and (7), one can have:

$$E = (RT/F)\ln(c_a^o/c_c^o) = (RT/F)\ln[(2c - c_a^o)/c_c^o] \qquad (8)$$

If

$$T = 298K\ (25°C),$$
$$E = 0.0591\log[(2c - c_c^o)/c_c^o],$$
$$(2\,c - c_c^o)/c_c^o = 10^{E/0.0591} = A$$
$$2\,c - c_c^o = A\,c_c^o$$
$$c_c^o = [2/(1 + A)]\,c$$
$$c_c^o = k'c$$
$$k' = 2/(1 + 10^{E/0.0591})$$
$$i = k\,(c - c_c^o)$$
$$i = kc\,(1 - k')$$

and as

$$kc = i_d,\ i = i_d\,(1 - k).$$

As one see easily, near the end point, the current varies linearly with concentration.

If the potential ΔE imposed between the two electrodes in a solution containig I_3^- and I^- is large enough to produce a current depending only on diffusion to the electrode surface (but not so large to produce undesirable reactions, e.g. 100 mV) the interpretation becomes similar to that for a single indicator electrode system. This can be visualized in Figure 1.

A potential change of about 10 mV (AA' in Figure 1) between the electrode is enough to produce a current flow across the cell, containing I_2 (actually I_3^-) and I^-, but in this case the current is given by:

$$i = k(c - c_c^o)$$

where: c = concentration of I in the bulk of solution

c_c^o = concentration of I at the electrode

In the diffusion layer, the concentration of I_2, c_c^o at 10 mV applied is not so small and, as the hydrodynamic conditions of the solution during stirring can suffer fluctuations, the titration will result in a curve. It is preferred, however, the use of 100 mV of potential change because under this condition one can have only the contribution of the diffusion current and the linearity response is extended. We have also verified experimentally that, when one substance of the reversible pair is present in a large excess, a better and more extended linearity is observed of current measured vs. concentration, with an increase in sensitivity.

According to these voltammetric (polarographic) considerations, it becomes clear why region 3 in Figure 3 is a straight line. The relation $[I^-]/[I_2]$ is so big that, practically, in the Nernst equation, in this condition, E is proportional to iodine (I_3^-) concentration only.

We consider that diffusion plays an important role in the biamperometric process and it is the basis for using biamperometry in trace analysis.

Objectives of This Work. According to what it is observed in the region 3 (Figure 3) we have decided to study the possibility of enlarging the linear range by varying some parameters. We studied two reversible systems: I_2/I^- and Br_2/Br^- and varied the applied voltage across the platinum electrodes, the concentrations of I_2, I^-, Br_2 and Br^- and the electrode area.

Experimental

a) The I_2/I^- System. An electrochemical vessel (Metrohm EA 875-20) and two platinum foil electrodes (1,0 cm^2 each) immersed in 20.00 cm^3 of a 0.50 M H_2SO_4 solution were used. The following potential were applied: 10, 30, 40, 50, 60 and 100 mV. The following initial molar ratios of $[I]/[I_2]$ were tested: 100, 1000 and 2000; this initial molar ratio was empirically established as the relation of mols of I^-/mols I_2 after 1.0 ml of KIO_3 solution was added to the KI solution in 0.5 M H_2SO_4. For the ratios 100, 1000 and 2000, the KI solutions were 0.015 M, 0.15 M and 0.30 M, respectively.

The experiments described were also made with platinum wire and platinum gauze electrodes to evaluate the effect of the area of platinum electrodes. A Sargent Welch III Polarograph was used for applying the potential and for measuring the current. A known amount of previously dried KI was weighted and added to the previously 20.00 cm^3 deaerated 0.50 M H_2SO_4 solution. With constant stirring of the solution, the galvanometer was set to zero and increasing volumes of 1.00 x 10^{-3} M KIO_3 were added to the solution. After the addition of IO_3^-, I_2 was formed in solution and the current was measured. The current, before ploting, was corrected by factor $(v + v_o) / v_o$, where v_o = initial volume and v = volume added.

The formation of I_2 results from:

$$IO_3^- + 5\,I^- + 6\,H^+ \rightleftharpoons 3\,I_2 + 3\,H_2O$$

b) The Br_2/Br^- System. In 20.00 cm^3 of a 1.5 M HCl solution, two platinum foils (1.0 cm^2 area each) were immersed into a Metrohm vessel (as above mentioned) and various potential were applied. The molar ratio $[Br^-]/[Br_2]$ was also varied. The following differences in potential were applied: 30, 50, 100, 200 and 400 mV. The molar ratio $[Br^-]/[Br_2]$ used were 10, 50, 100, 1000, 2000 and 4000 according to the same criteria used in $[I^-]/[I_2]$ previously. A 1.00 x 10^{-3} M $KBrO_3$ solution was used to produce Br_2 in the system. The formation of Br_2 results from:

$$BrO_3^- + 5\,Br^- + 6\,H^+ \rightleftharpoons 3\,Br_2 + 3\,H_2O$$

Results nd Discussion

According to the I_2/I^- system, as the amount of I is always much less than I_2, the amount of I^- is responsible for the appearance of the current. The Figures 5, 6 and 7 show that using 10 mV between the electrodes one has only the first four points in a straight line; using 30 mV with molar relation I^-/I_2 = 100 (Figure 5), one has six points on a straight line, while with a molar relation of 1000 and 2000 (Figures 6 and 7), one has seven points on a straight line. One can observe that in Figures 6 and 7 the slopes of the lines are higher than that of Figure 5. Using 40 mV across the electrodes, one has

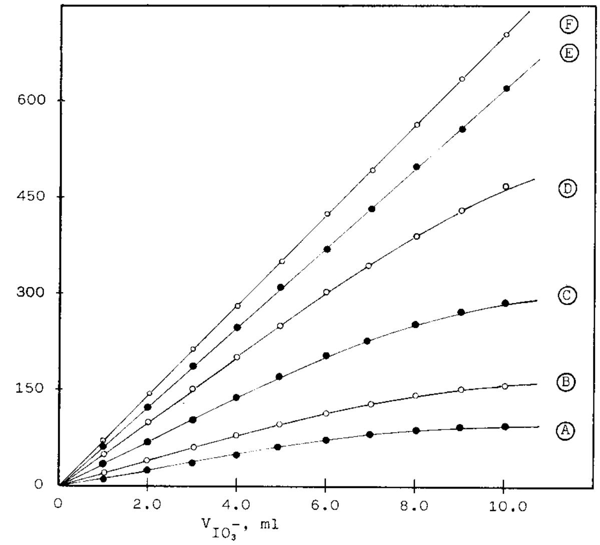

Figure 5. *Biamperometric measurements of current versus volumes of 10^{-3} M IO_3^- added in an acid solution containing I^- ions, under constant stirring. Platinum electrodes (1 cm^2 each). Molar relation I^-/I_2 = 100 after first volume added. A = 10 mV; B = 30 mV; C = 40 mV; D = 50 mV; E = 60 mV; F = 100 mV.*

seven or eight points on a straight line (Figure 5). With a molar relation I^-/I_2 equal 1000 and 2000 (Figures 6 and 7), the number of points in a straight line is about eight. Finally, from 60 mV onwards across the electrodes, even with a molar relation 100 (Figure 5), one has a straight line with more points, the same happening in Figures 6 and 7. As can be observed in Figure 5, on using 100 mV across the electrodes and a molar relation 100, the process is much more sensitive than at 60 mV. As the process, at 100 mV, has no other interference reaction, and at 100 mV one has he best conditions for the diffusion current, we decided to establish 100 mV.as the working potential, with the additional advantage that that at 100 mV the process is more sensitive than at 60 mV.

Other experiments were made, by fixing the potential across the platinum foils as 100 mV and varying the molar relation I^-/I_2 with the same empirical approach as in previous experiments. Using the same conditions as above mentioned, the following molar relation I^-/I_2 were used: 15, 25, 50 and 1000. It was verified that a larger straight line is obtained with a molar ratio $I^-/I_2 \geq 50$. Other series of experiments were made using platinum wire and platinum gauze electrodes. As expected, in the cases of platinum wire electrodes, in the same conditions as with platinum foils, the results were the same, but with lower sensitivity in all the cases, which is due to the lower area of the electrodes.

In the case of platinum gauze electrodes, as expected, was tremendously high due to the very large electrochemical area, but the relation between current (corrected) vs. concentration was not linear. This confirms the presence of a non-steady diffusion layer, forming and collapsing continuously. This phenomenon was commented previously. These results decided to use electrodes with 1.0 cm^2 area each as more convenient for achieving sensitivity and straight-lines.

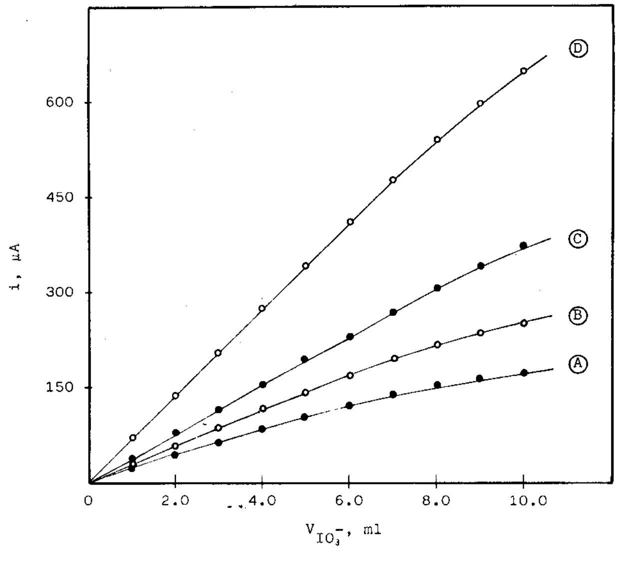

Figure 6. *Biamperometric measurements of current versus volumes of 10^{-3} M IO_3^- added in an acid solution containing I^- ions, under constant stirring. Platinum electrodes (1 cm^2 each). Molar relation I^-/I_2 = 1000 after first volume added. A = 10 mV; B = 30 mV; C = 60 mV; D = 100 mV.*

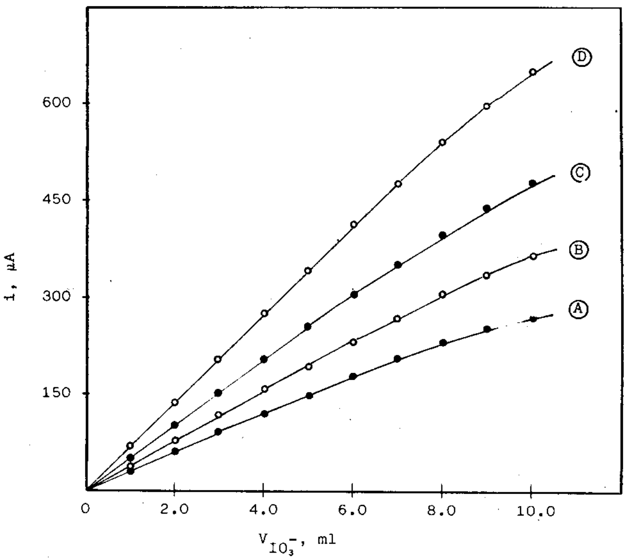

Figure 7. *Biamperometric measurements of current versus volumes of 10^{-3} M IO_3^- added in an acid solution containing I^- ions, under constant stirring. Platinum electrodes (1 cm^2 each). Molar relation I^-/I_2 = 2000 after first volume added. A = 10 mV; B = 30 mV; C = 60 mV; D = 100 mV.*

In the case of Br_2/Br^- system, one can see in Figure 8 and 9, that using, at least, 100 mV between the platinum electrodes and molar ratio Br_2/Br^- 2000 and 1.5 M HCl one concludes that perfect linear behavior is observed. We decided to establish the voltage as 300 mV to increase sensitivity; potentials higher than 300 mV are not recommended because the cathodic reduction of H takes place.

Concerning the dilution effect, we have verified that with effective and constant magnetic stirring of the solution a 15% dilution does not affect the straight line of current measurement (and corrected) vs. concentration. After 15% dilution, the straight line starts to curve.

Summarizing we can say that it is advisable to work as close as possible to the limit current, which gives the maximum possibility of diffusion process In this case one needs to work with the excess of one of the component of the redox pair. Using, for instance, the system described I^-/I_2, the potential across the platinum foils (1.0 cm each) should be 100 mV in a molar ratio $I^-/I_2 \geq 50$. In this conditions, $i = i_d = kC$, where C is the concentration of I_2 in the bulk of solution and i is the diffusion current. In Figure 1 the region DD' indicates the potential of 100 mV applied between the electrodes. If the potential would be 30 mV (BB') or 60 mV (CC'), the current value should be $i = k (C - c_{co})$, where C is the concentration of I_2 in the bulk of solution and C_{co} is the concentration of iodine in the diffusion layer. This latter

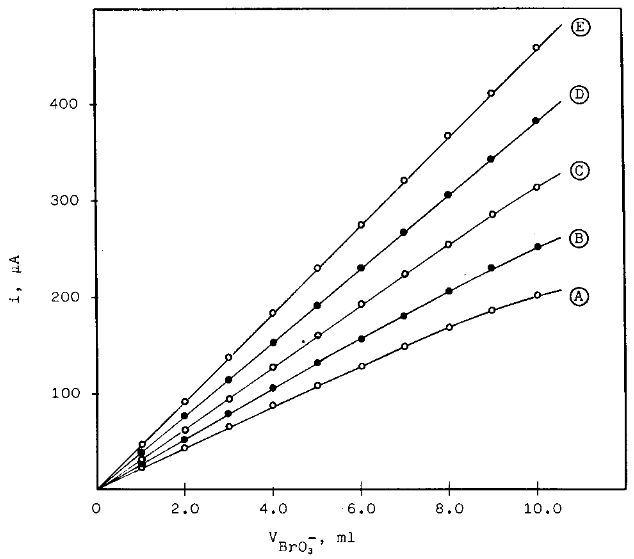

Figure 8. *Biamperometric measurements of current versus volumes of* 10^{-3} *M* BrO_3^- *added in 1.5 M HCl containing* Br^- *ions, under constant stirring. Platinum electrodes (1* cm^2 *each). Molar relation* $Br^-/Br_2 = 4000$ *after first volume added. A = 30 mV; B = 50 mV; C = 100 mV; D = 200 mV; E = 300 mV.*

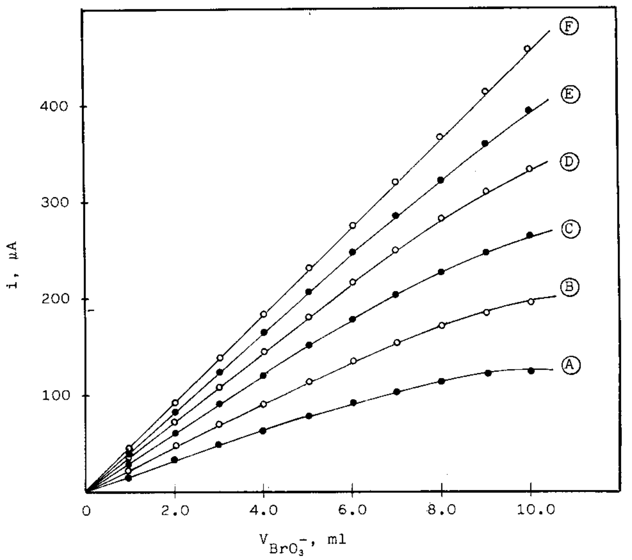

Figure 9. *Biamperometric measurements of current versus volumes of* 10^{-3} *M* BrO_3^- *added in 1.5 M HCl containing* Br^- *ions, under constant stirring. Platinum electrodes (1* cm^2 *each). V = 300 mV between the electrodes. Molar relation* Br^-/Br_2 *(after first volume added): A = 10 mV; B = 50 mV; C = 100 mV; D = 300 mV; E = 800 mV; F = 2000 mV.*

concentration is higher at 10 mV than at 30 mV and at 60 mV it is very small. One can understand easily the straight line obtained at 60 mV as shown in Figure 5.

Conclusions

Biamperometry has received little attention in the past probably because some considerations like "the rather limited reproducibility of current"[8,23,24], when the same volume of a solution is determined, which are not strictly correct. Of course it is difficult to obtain current reproducibility because of the occurrence of fluctuations in stirring and possibly in solution composition, when some samples of the original solution are analyzed. The approach proposed here, however, does not suffer from these limitations since the sample is analyzed in its own matrix, as illustrated by the results presented and discussed above. In other words, each volume of a sample can be determined with good precision and accuracy because some parameters to each sample are practically constant, mainly stirring. The authors referred[8,23,24] wanted unadequately compare biamperometry with amperometry.

According to our work, classical biamperometry can be transformed into a powerful analytical tool for accurate determinations as a result of the linear relation between concentration and current when one uses mainly a potential comprising the limiting current range for anodic and cathodic waves in reversible systems and when one uses an excess of one of the components. According to these considerations biamperometry can be used in trace analysis at ppb level, mainly when Pt foils (1.0 cm^2 each, for instance) can be used).

Biamperometry as proposed here can be used in both ways: (a) titration of (b) standard addition method, which broadens considerably the application of this technique.

These two approaches can be used in minutes with low cost equipment with 10 ppb levels determination with 10% precision. Around 10-12 determinations per hour can be performed manually. Another advantage is that, considering that the use of I_2 and Br_2 cover the majority of the determinations by microcoulometric titrations, the biamperometric generation of I_2 or Br_2 *in situ* by using primary standard KIO_3 or $KBrO_3$ has lower cost that microcoulometric ones, which could make determinations by the latter, obsolete.

Environmental species at ppb level have been determined in our laboratories with good accuracy in about 10 minutes, including for example: SO_2, S^{2-}, NO_2^-, NO_3^-, BrO_3^-, CN^-, phenols, Mn^{2+}, aniline, mercaptans, orgnic sulphides, organic dissulphides, IO_3^-, I^-, Br^-, Se, As, Cr(VI), Sb(III), Co(II), Mo(VI) and Mo(V).

Recently, the biamperometric detection was used in F.I.A. for determination[25] of NO_2^- - NO_3^-, molibdenum[26] and acid[27]. The determination of NO_2^- - NO_3^-, Mo(VI) and Mo(V), soued to be less sensitive than ours which probably are connected to inadequate geometry of the cell. We intend to use a wall-jet cell which gives array sensititvity.

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Present Adress:

Dimas Augusto Morozin Zaia, Universidade Estadual de Londrina,86075-900 Londrina, PR, Brasil

José Pedro Serra Valente, Universidade Estadual Paulista, 18600-400 Botucatu, SP, Brasil

Maria Olimpia de Oliveira Rezende. DQFM/IFQSC - São Paulo, SP, Brasil

References

1. E. Salomon, *Z. Physik. Chem.* **24**, 55 (1987).
2. E. Salomon, *Z. Elektrochem.* **4**, 71 (1987).
3. W.Nernst, E.S. Merrian, *Z. Physik. Chem.* **59**, 235 (1905).
4. C.W. Foulk, A.T. Bawden, *J. Am. Chem. Soc.* **48**, 2045 (1926).
5. K. Fischer, *Angew. Chemie* **48**, 394 (1935).
6. G. Wernimont, S.J. Hopkinson, *J. Ind. Eng. Chem. Ed.* **12**, 272 (1943).
7. P. Delahay, *Anal. Chem. Acta* **4**, 635 (1950).
8. I.M. Kolthoff, *Anal. Chem.* **26**, n- 11, 1685 (1954).
9. P. Delahay, "*Instrumental Analysis*", The MacMillan Co. (1987).
10. R. Gauguin, G. Charlot, *Anal. Chim. Acta* **8**, 65 (1953).
11. H.L. Kies, *Anal. Chim. Acta* **10**, 161 (1954) .
12. G. Duyckaerts, *Anal. Chim. Acta* **8**, 57 (1953).
13. J.H. Bradbury, *Trans. Faraday Soc.* **49**, 304 (1953).
14. J.H. Bradbury, Trans. *Faraday Soc.* **50**, 959 (1954).
15. S. Vydra, J. Vorlicek, *Microchem. J.* **9**, 1 (1965).
16 R.G. Monk, K.C. Steed, *Anal. Chim. Acta* **26**, 305 (1962).
17. L. Florant-Daltroff, *Bull. Soc. Chim., France*, 1039 (1962).
18. S. Vydra, J. Vorlicek, *Talanta* **13**, 603 (1966).
19. A.J. Bard, *Anal. Chem.* **33**, 11 (1961).
20. T. Rabockai, *An. Acad. Bras. Cinc.*, **48**, n- 2, 215 (1976).
21. T. Rabockai, *Anal. Letters* **9**, n- 4, 341 (1976).
22. T. Rabockai, R.S. Gonalves, P.R. Janissek, J.J. Pedrotti, *An. Acad. Bras. Cinc.* **54**, n- 1, 123 (1982).
23. J.J. Lingane, "*Electroanalytical Chemistry*", 2 Ed., Interscience Publishers Inc., New York, 12 (1958)
24. K. Stulik, F. Vydra, "*Electrometric Titrations, with Two Polarizable Electrodes Involving Chelating Agents*", in Chelates in Analytical Chemistry, H.A. Flaschka and A.J. Barnard Jr., Ed. Marcel Dekker Inc., 2, 102 (1969)
25. M. Trojanowicz, M. Hulanicki, W. Matszewski, *Anal. Chim. Acta* **194,** 119 (1987).
26. M. Trojanowicz, M. Hulanicki, W. Matszewski, *Anal. Chim. Acta* **188**, 165 (1986).
27. W. Matszewski, M. Hulanicki, M. Trojanowicz, *Anal. Chim. Acta* **194**, 269 (1987).