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Potentiometric Flow Injection Analysis Based on Redox Reaction with Redox Potential Buffers

Hiroki Ohura*, Toshihiko Imato**

*Department of Applied Chemistry and Biochemistry , Faculty of Engineering, Kyushu Sangyo University, Matsukadai, Higashi-ku Fukuoka 813-8503, Japan.

**Department of Applied Chemistry, Graduate School of Engineering, Kyushu University , Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.

Abstract

This review summarizes a potentiometric flow injection method for the determination of several redox species by using both a redox potential buffer solution consisting of a redox couple such as Fe(III)-Fe(II), $Fe(CN)_6^{3-}$-$Fe(CN)_6^{4-}$ and bromide-bromine, and a platinum electrode or a combined platinum-bromide ion selective electrode. The analytical principle and advantages of the proposed method are described and several examples of its application are demonstrated.

Keywords Potentiometric flow injection analysis, redox species, potential buffer, redox electrode detector

1. Introduction

A redox titration is widely used for the determination of many redox species in the fields of chemical laboratory as well as chemical industry. Flow injection analysis (FIA) [1] has been applied to titrimetric analyses in order to shorten and simplify the tedious and time-consuming procedures. We have proposed a potentiometric flow injection titration method for the determination of redox species by using a redox reaction of a sample with a potential buffer solution consisted of a redox couple such as Fe(III)-Fe(II), Ce(IV)-Ce(III) and $Fe(CN)_6^{3-}$-$Fe(CN)_6^{4-}$. The proposed method is based on the detection of change in the composition of the potential buffer solution due to a reaction of a redox sample with the potential buffer. Some similar papers to our method have already been published by Porter *et al*., Brunt and Karlberg with respect to the determination of redox species by potentiometry where they employed a redox reaction in an FIA system. For example, Porter *et al.* [2] and Brunt [3] have studied determinations of glucose and other reducing sugars based on the changes of redox potentials of hexacyanoferrate(III)-hexacyanoferrate(II) buffer solution caused by the reaction of sugars with $Fe(CN)_6^{3-}$. Karlberg *et al.* [4] have reported on an FIA of Fe(II) and ascorbic acid by means of a reaction with a stream of cerium(IV) solution and a redox electrode detector. These potentiometric detections for compounds have been performed with only use of oxidant without reductant as the stream of reagent solution in their flow systems. We employed the potential buffer consisting of the redox couple in order to stabilize the potential of the redox electrode.

The advantages of our proposed method using the potential buffer are as follows:

(1) the potential of the redox electrode is very stable and is reproducible in the potential buffer solution even at low concentrations, since the electrode is immersed in a well-defined potential buffer,

(2) the potential change is nearly proportional to the concentration of sample, although the potential change of the electrode is not so large,

(3) samples in a wide concentration range are determinable by appropriately selecting a concentration of the buffer solution.

In this review, the methodology of the proposed method, where an equilibrium potential after completion of a redox reaction between a sample and one of a redox couple of the potential buffer was utilized, was described together with several analytical examples. We also discussed the analytical results for redox compounds with use of the some potential buffers.

2. Principle of potentiometric flow injection method using potential buffer [5]

A typical two-channel flow system for determinations of redox species is shown in Fig. 1. The flow-injection apparatus consisted of a peristaltic pump, a sample injector, a flow-through type redox detector equipped with a platinum plate electrode and a silver/silver chloride reference electrode, a potentiometer for measuring the potential of the electrode detector.

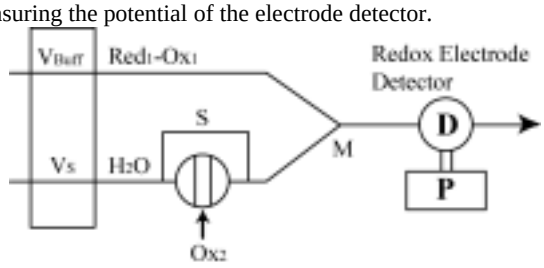

Fig. 1 Manifold for the FIA of oxidative and reductive species using a potential buffer solution. Red_1-Ox_1, redox couple (reductant and its oxidant); Ox_2, oxidative sample; M, confluence point D, flow-through type redox electrode detector; S, sample injector; P, potentiometer; V_{Buff} and V_S are flow rates of a buffer solution and water, respectively.

A potential buffer solution consisted of a redox pair, oxidant, Ox_1, and reductant, Red_1, is pumped through one channel at a flow rate of V_{Buff}. If an oxidative species, Ox_2, as a sample is injected into the other channel, where water is pumped at flow rate of V_s, as a carrier and is mixed with the potential buffer solution, the following redox reaction occur in the FIA system:

$$Ox_2 + mRed_1 \rightarrow Red_2 + mOx_1 \qquad (1)$$

where m is the number of moles of Red_1 required to reduce 1 mole of Ox_2. The potential of the redox electrode (E_1 in volt) is governed by the concentration ratio of the potential buffer solution and is expressed by

$$E_1 = E^o + (0.059/n) \log([Ox_1] / [Red_1]) \quad (25\ ^oC) \qquad (2)$$

where E^o is the formal redox potential, and n is the number of moles of electrons involved in the reaction, and $[Ox_1]$ and $[Red_1]$ are the concentrations of Ox_1 and Red_1, respectively. The baseline potential, E_1 (the potential when a sample is not injected), is written in terms of the initial concentrations of Ox_1 and Red_1, based on Eq. (2). In the case that the sample, Ox_2, is injected into the water stream, the redox potential, E_2, can be expressed as follows under the assumption that reaction (1) is complete before the sample zone reaches the detector when flow rates of V_{Buff} and V_S are equal.

$$E_2 = E^o + (0.059/n) \log\{([Ox_1] + m[Ox_2]) / ([Red_1] - m[Ox_2])\} \quad (3)$$

Where $[Ox_2]$ is the initial concentration of Ox_2. Under the assumption that no dispersion of the sample and reaction products occur while flowing through the manifold, potential change ($\Delta E = E_2 - E_1$), can be derived from Eqs. (2) and (3).

$$\Delta E = (0.059/n) \log\{(1 + m[Ox_2]/[Ox_1]) / (1 - m[Ox_2]/[Red_1])\} \quad (4)$$

The relationship between ΔE and $[Ox_2]$ depends on both the initial concentration ratio of Ox_1 to Red_1 and the value of m, as can be estimated from Eq. (4). Fig. 2 shows the effect of the molar ratio of $[Ox_1]$ to $[Red_1]$ in the potential buffer based on Eq. (4), when the both values of m and n are equal to 1. As shown in Fig. 2, the variation of ΔE with $[Ox_2]$ becomes relatively linear in a wide concentration range of Ox_2 within ca. 40 mV, when the value of $[Ox_1]$ / $[Red_1]$ is about 0.5. When $[Ox_1]$ / $[Red_1]$ is larger than 2 or less than 0.2, the sensitivity increases, but the shapes of curves become concave or convex, respectively. Thus, the potential change and baseline potential of the redox electrode are governed by the composition change of the redox couple in the potential buffer solution, according to Eq. (4). The linear relationship can be utilized as a calibration curve for the Ox_2 sample. However, the upper limit of measurable concentration of Ox_2 is limited by the concentration of the potential buffer. In other words, the measurable concentration range of Ox_2 can be controlled by selecting the concentrations of the potential buffer. The potential change is recorded as a peak-shaped signal, and the Ox_2 concentration is evaluated by the peak height.

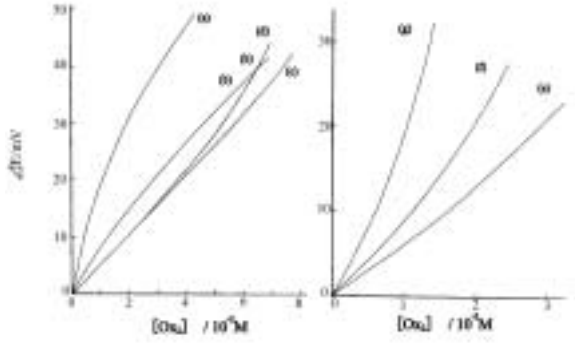

Fig. 2 Theoretical calibration curves calculated from Eq. (4). $[Red_1] + [Ox_1] = 0.2$ M, m = n = 1, Molar ratio of $[Ox_1] / [Red_1]$: (a) 0.05, (b) 0.2, (c) 0.5, (d) 1, (e) 2, (f) 4, (g) 9.

Furthermore, in the proposed FIA system, potential change, ΔE, is influenced not only by the concentration of the sample but also by the dispersion of the sample zone in the flow system. However, the degree of dispersion can be precisely controlled by an appropriate adjustment of the flow condition. Hence, the peak height is expected to be proportional to the concentration of Ox_2.

The theoretical potential change for a reductive sample is expected by changing the signs in front of m of Eq. (4) opposite.

3. Potential response of redox electrode in potential buffer solution consisted of a redox couple [5]

For the proposed method, a potential buffer solution consisting of a pair of a redox couple is desirable to be reversible electrochemically and to obey the Nernst equation. The reactivity of a redox sample with one of the redox couple in the potential buffer can be estimated by the order of the magnitude of E^o of the redox couple in the potential buffer. Indeed, we examined the reversibility and stability of several potential buffers in the flow system. The redox electrode showed the Nernstian response to an Fe(III)-Fe(II) couple (E^o = 0.77 V vs. NHE) and a Ce(IV)-Ce(III) couple (E^o = 1.68 V) in an acidic solution, and to an $Fe(CN)_6^{3-}$-$Fe(CN)_6^{4-}$ couple (E^o = 0.36 V) in an basic solution in the range of concentration ratio of the oxidized form to the reduced form from 0.1 to 10 in the each redox couple, according to Eq. (2). Especially, the redox electrode showed the Nernstian response in $Fe(CN)_6^{3-}$-$Fe(CN)_6^{4-}$ potential buffer even in lower concentration down to 10^{-5} M. On other hand, the redox electrode did not show a stable potential to Cr(VI)-Cr(III) and Mn(VII)-Mn(II) couples which are usually employed as a titrant of redox titrimetry. In the case of the Mn(VII)-Mn(II) couple, when the concentration of the couple became higher than 10^{-3} M, the precipitation of MnO_2 occured. This may be due to the fact that disproportionation reaction occurs in the mixed solution of the redox couple.

4. Analyses of hydrogen peroxide and ethanol in alcoholic beverages utilized Fe(III)-Fe(II) potential buffer [6-8]

For process control in production of hydrogen peroxide and industry of pulp and semi-conductor, the determination of concentrated hydrogen peroxide is desired. An analyte at high concentration can be determined by utilizing the controlled dispersion of a sample zone in the flow system. Since the Fe(III)-Fe(II) couple has a moderate redox potential, the determination of hydrogen peroxide was performed by using the Fe(III)-Fe(II) couple in acidic solution as the potential buffer, according to Eq. (5).

$$H_2O_2 + 2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \quad (5)$$

The determination of concentrated hydrogen peroxide up to ~10 M (30 %) was achieved successfully by using a 0.4 M Fe(III)-0.4M Fe(II) potential buffer containing 1M H_2SO_4, where the sample could be diluted by ca. 80-fold by reducing

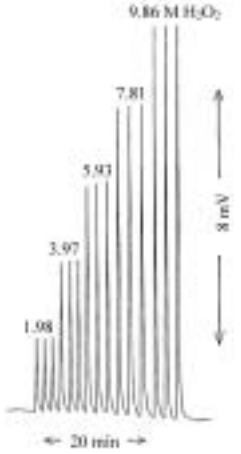

Fig.3 Calibration peaks for a concentrated aqueous solution of hydrogen peroxide.

the injected sample volume to 1μl. The calibration peaks for concentrated hydrogen peroxide are shown in Fig. 3. Even in such a high dispersion system, the R.S.D for the determination of 9.86 M H_2O_2 was 0.7 % (n=10). The proposed method could be used in the on-line monitoring of the production of hydrogen peroxide, as well as for bleaching and washing processes where concentrated hydrogen peroxide is used.

The selective determination method of ethanol in alcoholic beverages (Japanese sake, beer, wine, whisky and shochu) has been developed by using the Fe(III)-Fe(II) potential buffer solution and a gas-diffusion unit equipped with a membrane. The flow injection manifold equipped with a gas-diffusion separation is shown in Fig. 4. The gas-diffusion separation unit comprises two Daiflon blocks furnished with a shallow groove (37 mm long, 3mm wide, 0.5 mm deep) and separated by a porous poly (tetrafluoroethylene) (PTFE) membrane, which allows transfer of ethanol from a stream of C.S. to a stream of $R.S._1$. The PTFE membrane is 50 μm thick and 0.4 μm of pore size. The method was based on the detection of the composition change of the Fe(III)-Fe(II) couple in the potential buffer, which was caused by the reduction reaction of acidic dichromate with ethanol permeated through a membrane as vapor. The PTFE membrane for separation of alcohol was more excellent than a poly(substituted-acetylene)/polysiloxane graft copolymer membrane, because of high permeability of alcohol and simplicity of the manifold. The flow injection peaks for calibration curve were obtained in the concentration range from 3 to 40 %(v/v) ethanol contents. Sampling rate of ~25 h^{-1} was possible under the flow condition indicated in Fig. 4. Analytical results of ethanol contents in alcoholic beverages using the proposed method were in good agreement with those obtained by a gas-chromatographic determination. However, when the FIA technique without the gas-diffusion separation unit was applied, positive errors of 20 – 30 % were observed for Japanese sake, beer and wine. This may be due to the presence of aminoacids and other organic acids in the alcoholic beverages.

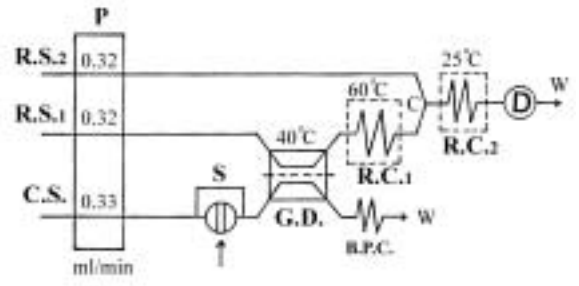

Fig. 4 Flow-injection manifold equipped with gas-diffusion separation unit for determination of ethanol.
C.S., carrier (H_2O): $R.S._1$, reagent solution (0.015 M $K_2Cr_2O_7$, 2 M H_2SO_4); $R.S._2$, reagent solution (0.135 M $FeSO_4(NH_4)_2SO_4$); S, sample injector (140 μl); G.D., gas-diffusion unit; $R.C._1$, reaction coil (1m, 0.5 mm); $R.C._2$,reaction coil (2m, 0.5 mm); B.P.C., back pressure coil (10m, 0.5 mm)

5. Analyses of reducing sugars, amylase and manganese(II) utilized $Fe(CN)_6^{3-}$-$Fe(CN)_6^{4-}$ potential buffer [9-14]

The redox couple of $Fe(CN)_6^{3-}$-$Fe(CN)_6^{4-}$ has a lower redox potential as 0.36 V and is known to show unique redox behavior to reducing sugars. The redox electrode shows a stable potential to the $Fe(CN)_6^{3-}$-$Fe(CN)_6^{4-}$ couple in alkaline media, but is not stable in neutral to acidic solution because auto-oxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ occur in such media. The analytical method for the determination of reducing sugars was based on the detection of change in the composition of the $Fe(CN)_6^{3-}$-$Fe(CN)_6^{4-}$ couple in the reaction of reducing sugar with of $Fe(CN)_6^{3-}$ in alkaline solution, according to Eq. (6).

$$\text{Reducing sugar} + m\,Fe(CN)_6^{3-} \rightarrow m\,Fe(CN)_6^{4-} + \text{other products} \quad (6)$$

where m is the number of moles of $Fe(CN)_6^{3-}$ required to oxidize a mole of reducing sugar.

The concentration of NaOH in the potential buffer and reaction temperature, as a standard procedure in flow system were 0.6 M and 85 °C, respectively. For example, in the case for the determination of glucose [10], other products by Eq. (6) were reported to be gluconic and glucanic acids and the reaction time completed in about 2.5 min. The sample in the concentration range from 10^{-7} M to 10^{-3} M at injection volume of 140 μl could be determined by changing the concentration of the $Fe(CN)_6^{3-}$-$Fe(CN)_6^{4-}$ potential buffer solution from 1 x 10^{-5} M to 1 x 10^{-2} M. The relationship between the measurable concentration range of glucose and the concentration of potential buffer is shown in Table 1. For the 1 x 10^{-5} M $Fe(CN)_6^{3-}$ - $Fe(CN)_6^{4-}$ potential buffer, fluctuation and drifts of a baseline potential were within 0.3 mV and less than 0.8 mV/h, respectively, and the detection limit was 0.1 μM. When the concentration of the potential buffer was lower than 5 x 10^{-6} M, the drift and fluctuation of the baseline potential became larger, and peak heights were not reproducible.

Table 1 Effect of concentrations of $Fe(CN)_6^{3-}$-$Fe(CN)_6^{4-}$ potential buffer solution on sensitivity

Concentration (M)	Sensitivity [a] (mV mM^{-1})	Measurable concentration range (M)
1 x 10^{-2}	9.7	2.0 x 10^{-4} ~ 1.8 x 10^{-3}
1 x 10^{-3}	9.5 x 10	2.0 x 10^{-5} ~ 1.8 x 10^{-4}
1 x 10^{-4}	9.4 x 10^2	2.0 x 10^{-6} ~ 1.8 x 10^{-5}
5 x 10^{-5}	1.9 x 10^3	1.0 x 10^{-6} ~ 1 .0 x 10^{-5}
1 x 10^{-5}	6.2 x 10^3	2.5 x 10^{-7} ~ 2.5 x 10^{-6}

a) Sensitivity: slope of calibration curve (peak height/mV obtained by injection of 1 mM glucose)

The other reducing sugars (2-deoxy-D-ribose, L-rhamnose, D-ribose and D-mannose as monosaccharides, and cellobiose, maltose and lactose as disaccharides) were also determined by the same potential buffer [9]. Sensitivities of monosaccharides were generally lower than those of disaccharides. The separate determination of mixed reducing sugars was achieved by combining proposed FIA method with HPLC as a post column technique [11]. In this case, sugars were converted to borate complexes by using a borate solution as an eluent and were separated by an anion-exchange column. The lower detection limit of reducing sugars was as low as 0.4 - 2.0 μM for injection of 20 μl sample. The proposed potentiometric method provides the similar or higher sensitivity compared to those of amperometric, fluorometric, and spectrophotometric detection methods. Furthermore, a simultaneous determination of sucrose and glucose was conducted by using the proposed FIA method incorporated a bypass coil connected with an invertase-immobilized column in parallel [12].

As the application for determination of reducing sugar, the determination of amylase activity [13] was carried out by utilizing the redox reaction of $Fe(CN)_6^{3-}$ with reducing sugar, which was produced from the enzymatic hydrolysis reaction (pH: 5.0, 37 °C) of starch with amylase. The determination of 15 samples/h was possible with good reproducibility, although it took about 6 min from sample injection to detection of a peak maximum in the present flow system. Amylase in a wide activity range (10^{-2} U ml^{-1}-10^{-4} U ml^{-1}) could be determined by selecting the concentration of the potential buffer (10^{-3} M – 10^{-5} M). This method was successfully applied to the determination of amylase in some commercial digestive medicines containing amylase with an accuracy of 4.5 % - 8.7 % compared with analytical

results obtained using the official titrimetric method (modified Somogyi method).

The determination of metal ions such as manganese (II) and cobalt (II) was found to be possible by the same $Fe(CN)_6^{3-}$-$Fe(CN)_6^{4-}$ potential buffer as for reducing sugars [14]. However, the reactivity of $Fe(CN)_6^{3-}$ with manganese (II) and cobalt (II) is quite different in pH media and the reactivity of of $Fe(CN)_6^{3-}$ with manganese (II) is much higher than that with cobalt (II). Therefore, the selective determination of manganese (II) in the presence of cobalt (II) at concentration of 50-fold that of manganese (II), could be achieved by selecting reaction condition near pH 8. Manganese (II) in soils is known to be one of essential components on the growth of plants, so the determination of manganese (II) in soil sample collected from tea field was conducted by using the potential buffer in neutral media (pH: 8.2) containing ammonium citrate solution. As a result, the lower detection limit and sampling rate of the proposed method was 1 x 10^{-7} M (5.5 ppb Mn) and 20h^{-1}, respectively. The proposed method provides the almost same sensitivity compared with the other flow injection technique. The analytical results for the determination of manganese (II) in soil of tea field obtained by the proposed method was in good agreement with that obtained by atomic absorption spectrometry.

6. Analysis of phenol utilized a bromine-bromide potential buffer and a combined platinum electrode with bromide ion-electrode [15, 16]

The determination of phenol [15] was carried out by using a bromination reaction with a bromine-bromide potential buffer solution, where a combined electrode detector consisted of a bromide ion-selective electrode and a platinum electrode was used for detecting the change in the bromine concentration in the buffer solution. The bromination reaction is expressed by Eq. (7).

$$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr \qquad (7)$$

When the bromination reaction completes according to Eq. (7), the potential change (ΔE) of the combined electrode is expressed by the following equation.

$$\Delta E = 0.059 \log\{([Br_2] - [C_6H_5OH]) / [Br_2]\} \qquad (8)$$

Where, $[Br_2]$ and $[C_6H_5OH]$ are initial concentrations of Br_2 and phenol, respectively. The theoretical calibration curve for phenol calculated from Eq. (8) became concave. However, assuming a second-order reaction between phenol and bromine in acidic solution, the relationship between ΔE and $[C_6H_5OH]$ is approximately linear, when the amount of bromine reacted is less than ca 40 % of the initial concentration of bromide. The flow system for the determination of phenol and calibration peaks are shown in Fig. 5. The analysis was conducted by utilizing the detection of the transient potential change at an initial stage of the bromination of phenol in a flow system.

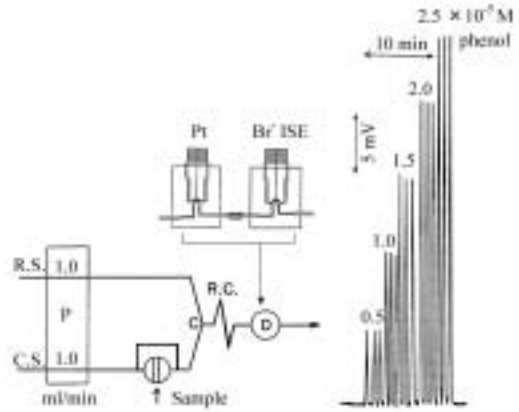

Fig. 5 FIA system for the determination of phenol and calibration peaks.
C.S., carrier (H_2O): R.S.$_1$, reagent solution (1 x 10^{-5} M Br_2- 0.4 M Br^-, 0.2 M H_2SO_4); R.C., reaction coil (80 cm, 0.5 mm i.d.); D, combined electrode detector (platinum electrode and solid-state bromide ion-selective electrode)

As can be seen from Fig. 5, a linear relationship between peak signals and phenol concentration was observed in the range of 5 x 10^{-6} M to 2.5 x 10^{-5} M. The proposed method was also possible the determination of other phenols such as *p*-nitrophenol, *p*-chlorophenol, β-naphthol and *m*-cresol, and was further applied to the separate determination of phenols by combining the proposed FIA method with HPLC, as a post column technique [16].

7. Conclusion

The methodology of our proposed method for flow injection determination of redox compounds by using the potential buffer and the redox electrode detector was described. The method could be useful for application to various analyses in process control and in environmental monitoring. The method is predicted to be subject to some redox species as existed in analyte sample, judging from the principle of the method, if the redox species react with the component of the potential buffer. However, the applicability of the proposed method could be possibly expanded by equipping an effective scavenger column in the flow system for eliminating interfering substance.

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