Potentiometric Flow Injection Determination of Redox Compounds by Using Potential Buffers

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Our proposed potentiometric flow injection determination method of redox species by using both a redox potential buffer solution and redox electrode detection is reviewed. The principle, analytical characteristics and advantages of our proposed method are described and several examples of application of our method are given in this review.

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A flow injection injection analysis (FIA)1 is a promising method for a rapid volumetric analysis because of its high throughout. An FIA titrimetric method has been reported by many investigators.2–5 Pungor et al.2 have developed the "triangle-programmed titration technique" and applied it to an argentimetric titration. Ruzicka et al.3,4 have developed an FIA titration method based on measurement of peak widths. Astrom5 has reported a flow analysis method called "single point titration" by using both a glass electrode and a universal buffer solution, which was designed to give a linear pH-response to the sample concentration. We have proposed a method of spectrophotometric flow injection determination of acids and bases or metal ions by using reactions of a sample with a pH buffer or a metal buffer solution containing an indicator and applied it to for the potentiometric detection by using a glass electrode or a metal ion-selective electrode.6,7

We also proposed a potentiometric method of flow injection determination of redox species by using redox reactions of a sample with a potential buffer solution consisting of a redox couple, such as Fe(III)-Fe(II), Ce(IV)-Ce(III) and Fe(CN)6 3–-Fe(CN)6 4–. Some similar papers precedent to our method have been published by Porter et al.5, Brun1 and Karlberg8 with respect to the determination of redox species potentiometry employed a redox reaction in an FIA system. Their potentiometric detections for oxidized compounds have been performed with only use of oxidant not reductant as a stream of reagent solution in the flow system.

Our 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. The advantages of the proposed method using the potential buffer are as follows: (1) the electrode potential of the redox electrode is very stable and is reproduceable in the potential buffer even at low concentrations, since the electrode is immersed in a well-defined potential buffer, (2) the potential change is nearly linear against 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 selecting concentration of the potential buffer appropriately. The sensitivity of the proposed method can be enhanced by detecting a large transient potential change due to an intermediate species generated by the reaction of the sample with chloride or bromide added to the potential buffer. We have applied the proposed method to rapid and highly sensitive determination of redox compounds in real sample such as residual chlorine in tap water and hydrazine in boiler water etc.

In this paper, the analytical methodology of the proposed method was described for the both cases where an equilibrium potential reached after a simple redox reaction was measured, and a transient potential generated during a complexed redox reaction was measured. We discussed the analytical results for redox compounds with respect to the sensitivity for above two cases.

Analytical methodology

Use of the equilibrium potential after completion of redox reaction

A two-channel flow system is shown in Fig.1. A potential buffer solution consisted of a redox couple, oxidant, Ox1, and reductant, Red1, is pumped through one channel at a flow rate of VBuff. When an oxidative species, Ox2, as a sample is injected into the other channel, where water is pumped at a flow rate of Vs, as a carrier and is mixed with the potential buffer, the following redox reaction occurs in the FIA system:

\[ \text{Ox}_2 + n\text{Red}_1 \rightarrow \text{Red}_2 + n\text{Ox}_1 \] (1)

where n is the number of moles of Red1 required to reduce 1 mole of Ox2. The baseline potential (Ei V) (the potential when a sample is not injected), is written by Eq. (2) in terms of the initial concentrations of Ox1 and Red1.

\[ E_i = E^0 + 0.059 \log([\text{Ox}_1]/[\text{Red}_1]) \text{ (25 °C)} \] (2)

where E^0 is the formal redox potential, and [Ox1] and [Red1] are the concentrations of Ox1 and Red1, respectively. In the case that the sample, Ox2, is injected, the redox potential, Ei, can be expressed as follows under the assumption that reaction (1) is complete before the sample zone reaches the detector when flow rates of Vbuff and V, are equal.

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E₂ = E₀ + 0.059 log((n[Ox₁] + n[Ox₂]) / (n[Red₁] - n[Ox₂]))
(3)

where [Ox₂] is the initial concentration of Ox₂. Under the assumption that no dispersion of the sample and reaction products occurs, the potential change (ΔE = E₂ - E₁), can be derived from Eqs. (2) and (3).

ΔE = 0.059 log((1 + n[Ox₂]/[Ox₁]) / (1 - n[Ox₂]/[Red₁]))
(4)

The relation between ΔE and [Ox₂] varies with both the initial concentration ratio of Ox₁ to Red₁ and the value of n, as can be estimated from Eq. (4). A linear relationship holds between ΔE and [Ox₂], where ΔE is within ca. 25 mV, when the ratio of [Ox₁] / [Red₁] is unity. Thus, the linear relationship can be utilized as a calibration curve for the oxidative sample. The potential change is recorded as a peak-shaped signal, and the Ox₂ concentration is evaluated from the peak height. The same calibration curve is obtained for a reductant sample.

The potential change of the redox electrode are governed by the redox reactions. A potential buffer solution containing chloride or bromide as a function of time

The potential buffer consisting of a redox couple employed for the redox reaction are shown in Fig. 1. When an oxidative sample, Ox₂, injected into the carrier stream, the potential increases towards an equilibrium potential, according to Eq. (7) or (8), because the redox potential of chloride or bromide is much higher than that of the redox couple Ox₁/Red₁. After a short period, the potential decreases towards an equilibrium potential, according to Eq. (7) or (8). Therefore, transient response potential is a mountain-shaped, as shown in Fig. 2. Since the potential change, which is produced from the oxidative sample, is confirmed to be the first order to the concentration of Ox₂, the linear relationship between the potential change and the concentration of Ox₂ holds at any times interval from the start of the reaction (5) or (6). In order to obtaining higher sensitivity, the flow system is designed to detect the large transient potential change timely. Potential changes (peak signals) obtained at appropriate reaction time are proportional to the concentration of Ox₂.

Potential buffer solution

The potential buffer consisting of a redox couple employed for the proposed method is desirable to be reversible electro-chemically and to obey the Nernstian equation. The reactivity of redox reaction between a redox sample and the potential buffer can be estimated by the order of the magnitude of E₀ of the redox couple in the potential buffer. The redox electrode obeys the Nernstian response to an Fe(III)-Fe(II) couple (E₀ = 0.77 V) and a Cr(VI)-Cr(III) couple (E₀ = 1.68 V) in acidic solution, and an Fe(CN)₆³⁻-Fe(CN)₆⁴⁻ couple (E₀ = 0.36 V) in wide concentration ratio of the redox couple. Especially, the redox electrode was found to show the Nernstian response in Fe(CN)₆³⁻-Fe(CN)₆⁴⁻ 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. This may be due to the fact that disproportionation reaction occurs in mixed solution of the redox couple.

Analyses based on an equilibrium potential after completion of a simple redox reaction

The potential change of the redox electrode are governed by the composition change of the redox couple in the potential buffer solution, according to Eq. (4) as described in a previous section. The upper limit of measurable concentration of an analyte is limited by the concentration of the potential buffer. This limitation means that the concentration of the potential buffer should be chosen, depending on the concentration level of the analyte. However, the measurable concentration range can be expanded by appropriately selecting the concentrations of the potential buffer. Furthermore, 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 as the potential buffer. For process control in production of hydrogen peroxide and industry of pulp and semi-conductor, the determination of high concentration of hydrogen peroxide is desired. Hydrogen peroxide up to ~10 M (30 %) was successfully conducted by using a 0.4 M Fe(III)-0.4 M Fe(II) potential buffer containing 1 M H₂SO₄, where the sample could be diluted by ca. 80-fold by reducing the injected sample volume to 1 µl.12 Even in such a high dispersion system, the R.S.D for determination of 10 M H₂O₂ was 0.7 % (n=10). 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. Analytical results using the proposed method were in good agreement with those obtained by a gas-chromatographic determination. 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 alcohol vapor permeated through a membrane. The micro-porous poly(tetrafluoroethylene) 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.13,15

The redox couple of Fe(CN)₆³⁻-Fe(CN)₆⁴⁻ 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)₆³⁻-Fe(CN)₆⁴⁻ couple in alkaline media, but is not stable in neutral or acidic solution because auto-oxidation of Fe(CN)₄³⁻ to Fe(CN)₄⁵⁻ occurs in such media.

By utilizing a redox reaction of Fe(CN)₆³⁻ with glucose in alkaline media, glucose in the concentration range from 10⁻³ M to 10⁻¹ M at injection volume of 140 µl could be determined by changing the concentration of the Fe(CN)₆³⁻-Fe(CN)₆⁴⁻ potential buffer from 1 x 10⁻⁵ M to 1 x 10⁻² M. The concentration of NaOH in the potential buffer and reaction temperature were experimentally determined at 0.6 M and 85 °C, respectively, as a standard procedure of analysis. The detection limit for glucose was 0.1 µM when the 1 x 10⁻⁵ M Fe(CN)₆³⁻ - 1 x 10⁻⁴ M Fe(CN)₆⁴⁻ potential buffer was used.15 When the concentration of the potential buffer was lower than 5 x 10⁻⁸ M, the drift and fluctuation of the baseline potential became larger, and peak heights were not reproducible. 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.16 The separate determination of mixed reducing sugars was achieved by combining the proposed FIA method with HPLC as a post column technique.17 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. As an application for determination of reducing sugar, the determination of amylase activity was carried out by utilizing the redox reaction of Fe(CN)₆³⁻ with reducing sugar, which was produced from the enzymatic hydrolysis reaction of starch with amylase. 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 commercial digestive medicines containing amylase with an accuracy of 4.5-8.7 % compared with analytical results obtained by using the official titrimetric method.18 The determination of metal ions such as manganese(II) and cobalt(II) was found to be possible by the same Fe(CN)₆³⁻-Fe(CN)₆⁴⁻ potential buffer for reducing sugars.19 Manganese(II) in soils is known to be one of essential components for 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 was 1 x 10⁻³ M and the proposed method provided the almost same sensitivity compared with the other flow injection technique. The analytical results for manganese(II) in soil of tea field obtained by the proposed method was in good agreement with those obtained by atomic absorption spectrometry.

The determination of phenol was carried out by using bromination reaction with acidic bromine solution in stream, where a combined electrode detector consisted of a bromide-selective electrode and a platinum electrode was used for detecting the change in the bromine concentration in the stream. A linear relationship between peak signals and phenol concentration was observed in the range of 5 x 10⁻⁶ M to 2.5 x 10⁻³ M.

### Analysis based on large transient potential change caused by a complex redox reaction

In an FIA system, a reaction time during reaction of a sample with a reagent can be easily controlled by using different coil lengths and/or different flow rates of the carrier and reagent streams. Therefore, the sensitivity enhancement would be expected if a transient potential change due to an intermediate generated from the reaction of an analyte with chloride or bromide can be detected timely in the flow system. Bromate has been utilized as bleaching agent for some food products, so that the sensitive determination of residual bromate in foods is desired for safety of the product. Then, we applied the determination of bromate to the proposed method.20 In a batch system, the time–course of the response potential after an addition of bromate to the Fe(III)-Fe(II) potential buffer with and without bromide was monitored. As a result, when the potential buffer without bromide was used, the mountain-shaped change was observed in a similar manner in Fig. 2, and the potential finally reached a constant equilibrium potential, which agreed with the values calculated according to Eq. (4). However, larger transient potential change as 20 - 30 mV was obtained for the 10⁻⁶ M order of bromate, when the 1 x 10⁻⁵ M potential buffer containing 0.4 M bromide was used. Since the maximum potential was observed in a short period after addition of bromate, the flow system was constructed to detect the maximum potential. As a result, the calibration for bromate was obtained in the level of 10⁻⁶ M with the sensitivity (mV/mM) of 6 x 10⁻⁵. This indicates that the sensitivity is enhanced 180 fold compared with that using the change in equilibrium potential. The detection limit (S/N=3) was 5 x 10⁻⁸ M.
The mechanism of the large transient potential change was explained qualitatively as follows: The initial potential is governed by the (Fe(III)-Fe(II)) ratio in the potential buffer based on Eq. (2). The potential raising observed just after the addition of bromate may be due to reaction (6) to generate the intermediate bromine, Br₂, which has a higher redox potential of Br⁺/Br⁻ couple (E° = 1.09 V) than that of (Fe(III)/Fe(II)) couple. The potential descending may be due to a decrease in bromine concentration by reaction of bromine with Fe(II), based on Eq. (8). The evidence that the large transient potential change with the mountain-shaped came from bromine as the intermediate, was confirmed by stopped-flow spectrophotometry.23

The other oxidative species such as chlorite, ozone, Cr(VI) and hydrogen peroxide could be also determined by detecting the large transient potential change caused by the same manner as for the case of bromate by using the Fe(III)-Fe(II) potential buffer containing bromide.22 The sensitivities obtained from FIA calibration peak increased in the order H₂O₂ < O₃ < Cr(VI) < ClO₂⁻ < BrO₃⁻. For the determination of hydrogen peroxide, the addition of ammonium molybdate to the potential buffer was found to accelerate the generation of bromine from the reaction of hydrogen peroxide with bromide. The detection limit for hydrogen peroxide was 4 x 10⁻⁷ M by using the 1 x 10⁻⁴ M Fe(III)-Fe(II) buffer containing 0.4 M NaBr, 1.0 M H₂SO₄ and 0.5 % (NH₄)₂MoO₄. This method was applied to the determination of hydrogen peroxide in rainwater.24 The determination of Cr(VI) in seawater was performed by using the Fe(III)-Fe(II) potential buffer containing bromide.25 Sequential determination of Cr(VI) and Cr(III) was achieved by combining a stream of Ce(IV) with the above flow system for Cr(VI).26

We found that a large transient potential change was also observed when oxochlorine species, ClO₃⁻, ClO₂⁻ and HClO was added to the Fe(III)-Fe(II) potential buffer containing chloride, although the magnitude of potential change was dependent on reactivity of oxochlorine. The analytical sensitivity for HClO and ClO₂⁻ obtained by the detection of the transient potential change in the FIA system was enhanced by ~700-fold compared with the sensitivity obtained by using an equilibrium potential. A simultaneous determination of ClO₂⁻, ClO₃⁻ or ClO₂⁻ · HClO was achieved by utilizing the difference in reactivity of oxochlorine species with chloride in the potential buffer.27 This method was applied to the determination of residual chlorine in a tap water sample.28 The determination of trace hydrazine was achieved by using an acidic Ce(IV)-Ce(III) potential buffer solution.29 The method is based on the measurement of a transient potential change, which was appeared in a negative direction. The shape of the transient potential change observed for hydrazine was different from that observed for bromate, Cr(VI) and oxochlorine. We estimate that the transient potential change is the potential shift from the Ce(IV)-Ce(III) couple to the N₂H₅⁺-N₂ couple, which electrode potential was much lower than that of the Ce(IV)-Ce(III) couple. Hydrazine in a wide concentration range from 10⁻⁵ M to 10⁻² M was determined by selecting the concentration of the potential buffer from 10⁻² M to 10⁻⁷ M, and detection limit was 1 x 10⁻⁷ M. The method was capable to apply to the determination of hydrazine in boiler water.

In 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 and several examples of application of the method were reviewed concerning mainly with respect to sensitivity enhancement. 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 coexisted in sample, judging from the principle of the method, if the redox species react with the component of the potential buffer. Equipping an effective scavenger column in the flow system for eliminating interfering substance could possibly expand the applicability of the proposed method.

References