Minireview

Sensitive Potentiometric Flow Injection Analysis of Redox Species Based on the Detection of an Intermediate Produced by a Redox Reaction with the Potential Buffer

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Abstract

This review summarizes a highly sensitive potentiometric flow injection method for the determination of various types of oxidative species, where a large transient potential change due to chlorine or bromine, generated during the reaction of the oxidative species with an Fe(III)-Fe(II) potential buffer containing chloride or bromide as an intermediate, is utilized. The analysis of trace amount of hydrazine based on the detection of a transient change in potential caused by the reaction of hydrazine with a Ce(IV)–Ce(III) potential buffer is also described.

Keywords: Sensitive potentiometric flow injection method, potential buffer containing bromide or chloride, intermediate

1. Introduction

In a previous minireview [1], we described a potentiometric flow injection analysis (FIA) method for the determination of redox species using a simple redox reaction of a sample with a potential buffer solution consisting of a redox couple such as Fe(III)-Fe(II), Ce(IV)-Ce(III) and $Fe(CN)_6^{3-}$-$Fe(CN)_6^{4-}$. This method is based on the detection of the change in potential of a redox electrode caused by a change in the composition of the potential buffer solution as the result of a reaction of the sample with the potential buffer. One of advantages of the method is that samples in a wide concentration range can be determined by selecting an appropriate concentration of the potential buffer.

The excellent characteristics of the FIA method permits its use in detecting a final product at an equilibrium state as well as of an intermediate in transient reactions before chemical equilibrium is reached, where an appropriate chemical reaction was used. Among the many redox reactions, there are several reactions where an intermediate compound with a short lifetime is generated. In such a case, the FIA method would be useful for detecting of the intermediate. During our research on the use of potentiometric FIA for the determination of redox species using the potential buffer, we discovered an interesting phenomena in which a large transient potential change of the redox electrode appeared, when a bromate solution was added to a Fe(III)-Fe(II) potential buffer containing bromide [2]. The large change in potential was found to be due to the fact that bromine, generated as an intermediate, was reduced to bromide by Fe(II) in the potential buffer. In the case of potentiometric FIA, if the electrode potential of the intermediate generated during the redox reaction of an analyte with the potential buffer is much higher than that of the potential buffer, a highly sensitive determination of the analyte could be achieved, if the intermediate in the FIA system could be detected. No report on a highly sensitive potentiometric FIA method for the determination of oxidative species in which the detection of an intermediate formed during a redox reaction has appeared, so far.

In this minireview, we describe a highly sensitive potentiometric FIA method based on the detection of a large transient potential change in the redox electrode, which appears a short period after mixing an analyte with the potential buffer. In the case where a Fe(III)-Fe(II) potential buffer is used, it was

found that the addition of bromide or chloride to the potential buffer enhances the sensitivity to various types of oxidizing species such as bromate, chrominum(VI), hydrogen peroxide and oxychlorine, etc. A high sensitivity to such oxidative species was obtained by the potentiometric detection of a large transient potential change due to the generation of intermediate bromine or chlorine during the reaction of the analyte with chloride or bromide in the potential buffer.

The advantage of the proposed method, in which the detection of an intermediate is involved, is that the bromide or chloride in the Fe(III)-Fe(II) potential buffer acts as an homogeneous catalyst for the formation of bromine or chlorine as an intermediate during a reaction process.

In this review, the mechanism of the transient potential change that influences sensitive and selectivity to the analytes of redox species is described together with several examples. The analytical results for the determination of oxidative species are discussed with respect to sensitivity.

2. Transient potential change generated by a redox reaction with Fe(III)-Fe(II) potential buffer containing bromide or chloride

The simple redox rection between oxidative species, Ox, and Fe(II) in sulfuric acid solution can be generally expressed as follow:

$$Ox + n\,Fe^{2+} + a\,H^+ \quad Red + n\,Fe^{3+} + b\,H_2 \qquad (1)$$
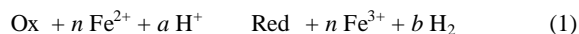
where n is the number of moles of Fe^{2+} required to reduce 1 mol of Ox, and a and b are stoichiometric coefficients.

If reaction (1) is complete, the potential change (ΔE in mV) of the redox electrode at 25 can be expressed by the Nernst equation, as described previously [1],

$$\Delta E = 59 \log\{(1 + n[Ox]_0/[\,Fe^{3+}]_0) \\ / (1 - n[Ox]_0/[\,Fe^{2+}]_0)\} \quad (mV, 25\ ) \quad (2)$$

where $[Ox]_0$, $[Fe^{3+}]_0$ and $[Fe^{2+}]_0$ are the initial concentrations of Ox, Fe^{3+} and Fe^{2+}, respectively. The variation of ΔE with [Ox] becomes relatively linear in the concentration range of Ox, where the ΔE is within ca. 20 mV, when the value of $[Fe^{3+}]_0$ /$[Fe^{2+}]_0$ is nearly equal to unity. The sensitivities, defined as the slope of the linear portion of the ΔE vs. [Ox] plot, are calculated to be 10.4, 20.9 and 31.3 mV mM^{-1} for $n = 2$, 4 and

6 respectively, from Eq. (2). These calculated values for sensitivity to several oxidative species are given in Table 1.

In batchwise experiment, in the case in which the Ox solution is added to an Fe(III)-Fe(II) potential buffer containing bromide or chloride, the response potential with a mountain-shaped transient change appears with increasing reaction time, as shown in Fig.1, although the concentration of Ox is lower by about three orders magnitude than that in the potential buffer without bromide or chloride. The transient potential change is due to the generation of bromine or chlorine as an intermediate formed by the reaction of Ox with bromide or chloride in the potential buffer.
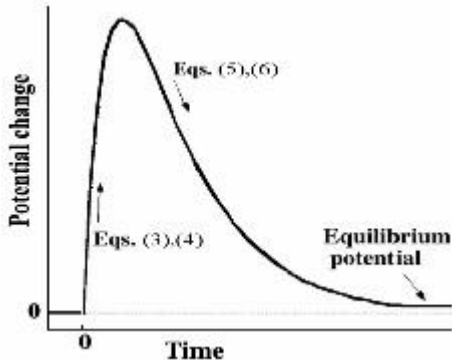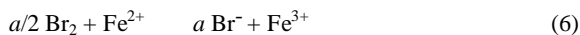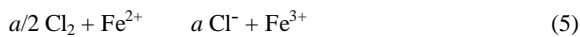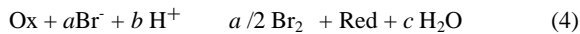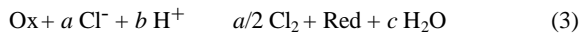

Fig. 1 Potential change during the reaction of Ox with an Fe(III)-Fe(II) buffer solution containing chloride or bromide as a function of time

The mechanism of the transient change in potential can be explained qualitatively by considering following reactions: Ox reacts first with chloride or bromide in the potential buffer and the reaction generates chlorine or bromine as the intermediate during the reaction process. Second, the intermediate (Cl_2 or Br_2) reacts with Fe(II) in the potential buffer. Thus, these reactions can be expressed by

$$Ox + a\,Cl^- + b\,H^+ \quad a/2\,Cl_2 + Red + c\,H_2O \qquad (3)$$

$$Ox + a\,Br^- + b\,H^+ \quad a/2\,Br_2 + Red + c\,H_2O \qquad (4)$$

$$a/2\,Cl_2 + Fe^{2+} \quad a\,Cl^- + Fe^{3+} \qquad (5)$$

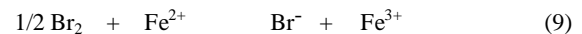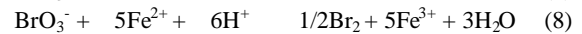$$a/2\,Br_2 + Fe^{2+} \quad a\,Br^- + Fe^{3+} \qquad (6)$$

where Red is the reduced form of Ox. For the mountain-shaped transient change, the initial potential is governed by the Fe(III)-Fe(II) ratio in the potential buffer. When Ox is added to the potential buffer, since Cl_2 or Br_2 is generated, the potential electrode is shifted from Fe(III)/Fe(II) to Cl_2/Cl^- or Br_2/Br^-. Since the redox potential of the Cl_2/Cl^- ($E^o = 1.33$ V) or Br_2/Br^- couple ($E^o = 1.09$ V) is much higher than that of the Fe(III)/Fe(II) redox couple ($E^o = 0.77$ V), the electrode potential is increased. The potential then decreases towards an equilibrium potential due to Eq.(5) or (6). The overall reaction which is the sum of elementary reactions (3) and (5) or of reactions (4) and (6), is given by Eq.(1) in equilibrium potential. That is, bromide or chloride in the potential buffer may act as a homogeneous catalyst for the formation and reduction of bromine or chlorine. The magnitude of the large transient potential change increases with decreasing concentration of Fe(III)-Fe(II) in the potential buffer components. This is due to the fact that the rate of reduction of bromine or chlorine by Fe(II), as expressed by Eq. (5) or (6), decreases.

In an FIA system, the reaction time during the reaction of an injected sample with a flowing reagent can be easily controlled by using different coil lengths and/or different flow rates of the carrier and reagent streams. The concentrations of sulfuric acid, bromide or chloride and Fe(III)-Fe(II) in the potential buffer solution are also important factors in terms of enhancing

sensitivity. By studying these optimum analytical conditions for the highly sensitive determination of oxidative species, a two-channel flow system, carrier stream (H_2O) and reagent stream (Fe^{3+}-Fe^{2+}, NaBr or NaCl in H_2SO_4 solution), was designed to detect the large transient potential change in a timely manner, where the maximum appears transiently. The flow-injection apparatus was the same as that shown in Fig. 1 in the previous minireview [1], except for the use of a gold plate electrode. The potential changes (peak signals) obtained at appropriate reaction times were proportional to the concentration of oxidative species.

3. Analysis of bromate using Fe(III)-Fe(II) potential buffer containing bromide [2-4]

Bromate is employed as bleaching agent for some food products, and is known to be generated as a by-product in water purification processes. Thus, the sensitive determination of residual bromate in foods or tap-water would be desirable for safety of food products and water quality. In a batch system, the time - course of the response potential after the addition of bromate to a potential buffer consisting of Fe(III)-Fe(II) containing bromide showed a mountain-shaped form, as shown in Fig. 1. The transient potential process can be expressed by following reactions.

$$BrO_3^- + 5Br^- + 6H^+ \quad 3Br_2 + 3\,H_2O \qquad (7)$$

$$BrO_3^- + 5Fe^{2+} + 6H^+ \quad 1/2Br_2 + 5Fe^{3+} + 3H_2O \qquad (8)$$

$$1/2\,Br_2 + Fe^{2+} \quad Br^- + Fe^{3+} \qquad (9)$$

The overall reaction, which is the sum of elementary reactions (7), (8) and (9), is given stoichiometrically based on Eq. (1). The equilibrium potential agreed well with the value (31.3 mV, Table 1) calculated from Eq. (2). A maximum transient potential change of 20 - 30 mV was obtained for a 10^{-6} M concentration of bromate, when a 1×10^{-2} M potential buffer containing 0.4 M bromide and 1 M sulfuric acid was used. A flow system was then designed to detect the maximum potential. As a result, a linear calibration for bromate was obtained at a level of 10^{-6} M with a sensitivity (mV/mM) of 10.6×10^3. This sensitivity was enhanced by 338 fold compared with that using the change in equilibrium potential, as shown in Table 1. The detection limit (S/N = 3) was 5×10^{-8} M. The sampling rate was ca. 35 samples/h.

Table 1 Sensitivities to oxidative species

Oxidative Species	Sensitivity (mV/mM)		Enhancement factor, (A)/(B)
	(A) Observed in FIA system	(B) Calculated [a]	
BrO_3^-	10.6×10^3	31.3 (n=6)	338
$Cr_2O_7^{2-}$	2.6×10^3	31.3 (n=6)	83
H_2O_2	2.5×10^2	10.4 (n=2)	24
ClO_2^-	6.9×10^3	20.9 (n=4)	339
O_3	8.0×10^2	10.4 (n=2)	77

a: Sensitivity calculated from Eq. (2)

The evidence that the origin of the large transient potential change with a mountain-shaped form was the formation and reduction of bromine as an intermediate, was confirmed by stopped-flow spectrophotometry. The change in absorbance at 447 nm was used for the determination of bromine. The time course for the absorbance change during the reaction among BrO_3^-, Fe^{2+} and Br^- in sulfuric acid solution showed a mountain-shaped form, and simulated that calculated from an equation of a successive first order reaction using the rates of reactions in (7), (8) and (9).

Furthermore, the equilibrium potential via the transient potential change was nearly equal to the initial potential because the concentration of Fe(III)-Fe(II) in the potential buffer was sufficiently higher than that of bromate in the sample, so that it was possible to reuse the potential buffer solution as a reservoir solution in a recycling (closed-loop) FIA (CFIA) system, as shown in Fig.2. As a result, the numbers of repetitive determinations, in which relative sensitivities within 5% were regarded as acceptable, were ca. 4000 and 2000 for the use of only 100 ml of 1×10^{-2} M and 1×10^{-3} M Fe(III)-Fe(II) potential buffer, respectively [4]. If 100 ml of potential buffer were used in the two-channel FIA method [2], only 65 samples could be determined
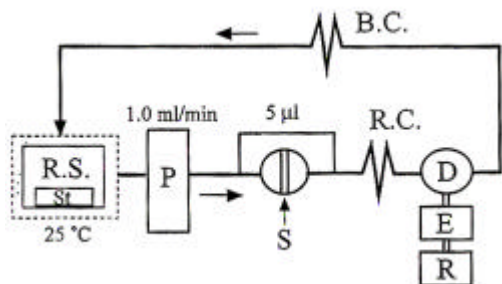

Fig.2 Schematic diagram of the CFIA system. RS, reservoir (100 ml, Fe(III)-Fe(II) 0.35 M NaBr and 0.2 % $(NH_4)_6Mo_7O_{24}$ in 1 M H_2SO_4); S, sample injection valve(5μ l loop); RC, reaction coil (13 cm); BC, back pressure coil(3 m); D, a flow-through type redox electrode detector equipped with a gold plate electrode and a silver/silver chloride reference electrode.

4. Analyses of harmonium(VI) and chromium(III) using Fe(III)-Fe(II) potential buffer containing bromide [5, 6]

In the case of the reaction of chromium(VI) with an Fe(III)-Fe(II) potential buffer containing bromide, the mechanism of the large transient potential change is due to the fact that bromine was generated by the reaction of bromide in the potential buffer with Cr(V), which was generated as an intermediate during the reaction of Cr(VI) and Fe(II) in the potential buffer. Thus, the transient potential process can be expressed by Eqs. (10) and (11). The decrease in potential after a maximum is explained by the progress of reaction (9), i.e., the bromine generated in the reaction (11) is consumed.

$$Cr(VI) + Fe^{2+} = Cr(V) + Fe^{3+} \qquad (10)$$

$$Cr(V) + 2Br^- \quad Cr(III) + Br_2 \qquad (11)$$
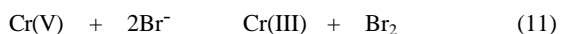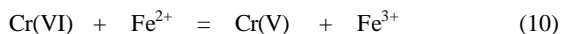
In the flow system, the detection of the large transient potential change was utilized for the determination of Cr(VI). As a result, the sensitivity to Cr(VI) was enhanced by 83 fold, compared with that in which the detection of the change in equilibrium potential was used. A detection limit of 2×10^{-8} M Cr(VI) was achieved by using a 1×10^{-4} M Fe(III)-Fe(II) potential buffer containing 0.4 M NaBr and 1.2 M H_2SO_4. Several heavy metal ions such as Cr(III), Cu(II), Zn(II), Ni(II) and Cd(II) did not interfere with the determination of Cr(VI) even in the case where their concentration was more than 10^2 times that of Cr(VI). It was possible to apply this method to the determination of Cr(VI) in seawater samples containing Cr(VI) at the 500 ppb level, the maximum permissible concentration in Japan.

The simultaneous determination of Cr(VI) and Cr(III) in a mixed sample of Cr(VI) and Cr(III) was performed with a three-channel flow system equipped with a six-way valve, as shown in Fig. 3. The six-way valve was used to switch the two reagent streams between the H_2SO_4 solution for the selective determination of Cr(VI) in the sample containing Cr(III) and

the Ce(IV) solution containing H_2SO_4 in order to oxidize Cr(III) to Cr(VI) by Ce(IV) for the determination of total chromium, the sum of Cr(VI) and Cr(III). The determination of Cr(III) in a mixed sample was obtained from the difference in peak height obtained by the two reagent streams. A linear calibration was obtained over the range of 1×10^{-6} M to 1×10^{-5} M for Cr(VI) and from 4×10^{-6} M to 4×10^{-5} M for Cr(III).
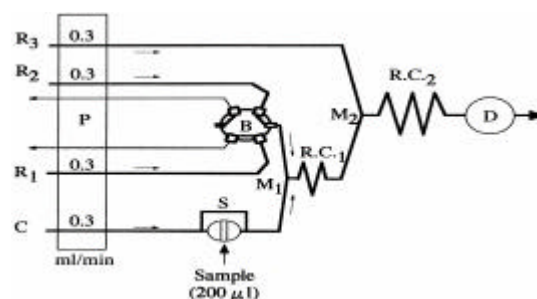

Fig. 3 Schematic diagram for the simultaneous determination of Cr(VI) and Cr(III). C, water or synthetic seawater; R_1, 0.05 M H_2SO_4; R_2, 2 $\times 10^{-4}$ M Ce(IV), 0.05 M H_2SO_4; R_3, 1×10^{-2} M Fe(III)-Fe(II) 0.6 M NaBr, 3.6 M H_2SO_4; B, switching valve.

5. Analyses of hydrogen peroxide and other oxidative species using Fe(III)-Fe(II) potential buffer containing bromide [7, 8]

In our previous minireview [1], the determination of high concentration of hydrogen peroxide by utilizing a large dispersion of a sample zone was demonstrated by using a stream of a Fe(III)-Fe(II) potential buffer without bromide. While the use of a stream of a Fe(III)-Fe(II) potential buffer containing bromide and Mo(VI) enhances the sensitivity to hydrogen peroxide. A highly sensitive determination of trace levels of hydrogen peroxide was achieved by detecting the large transient potential change due to the production of bromine as an intermediate. The oxidation of bromide to bromine by hydrogen peroxide occurred very rapidly with the assistance of Mo(VI) when Fe(II) was present in the potential buffer. The reaction mechanism of the transient potential change was estimated by batchwise experiments in which hydroxyl radicals, OH , were generated by the reaction of hydrogen peroxide with Fe(II) as an intermediate, and subsequently oxidized bromide to bromine. The elementary reactions for the transient process can be expressed by the following equations (12), (13) for the generation of bromine and Eq.(9) for the consumption of bromine. The overall reaction which is the sum of reactions (12), (13) and (9), is expressed by reaction (1)

$$H_2O_2 + Fe^{2+} + H^+ \quad OH + Fe^{3+} + H_2O \quad (12)$$

$$OH + Br^- + H^+ \quad 1/2Br_2 + H_2O \qquad (13)$$
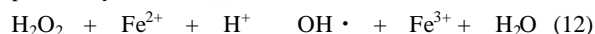
In the flow system, which utilized the detection of a large transient potential change, the sensitivity to hydrogen peroxide was enhanced by 24 fold compared with that obtained by the detection of the equilibrium potential, as shown in Table 1. The detection limit of 4×10^{-7} M (13.6 ppb) was achieved by using a 1×10^{-4} M Fe(III)-Fe(II) buffer containing 0.4 M NaBr, 1.0 M H_2SO_4 and 0.5% $(NH_4)_6Mo_7O_{24}$. This method was applied to the determination of hydrogen peroxide in rainwater.

Other oxidative species such as chlorite and ozone were also determined by the detection of large transient potential changes. The sensitivities to oxidative species examined in this work increased in the order $H_2O_2 < O_3 < Cr(VI) < ClO_2^- < BrO_3^-$, as shown in Table 1. This sequence of sensitivity

probably depends on the rate of reaction of oxidative species with bromide.

6. Analyses of residual chlorine and oxychlorine species using Fe(III)-Fe(II) potential buffer containing chloride [9, 10]

Since oxychlorines are considered to be hazardous to our health, the monitoring of levels of residual oxychlorines in drinking water is important for health safety. A large transient potential change was observed by the generation of chlorine based on Eqs.(14), (15) and (16) when oxychlorine species, ClO_3^-, ClO_2^- and HClO were added to a Fe(III)-Fe(II) potential buffer containing chloride, although the magnitude of the potential change was dependent on reactivity of the oxychlorines. It is noteworthy that the rate of reaction (16) was relatively slower than that of reactions (14) and (15).

$$HClO + Cl^- + H^+ \quad Cl_2 + H_2O \quad (14)$$

$$HClO_2 + 3Cl^- + 3H^+ \quad 2Cl_2 + 2H_2O \quad (15)$$

$$ClO_3^- + 5Cl^- + 6H^+ \quad 3Cl_2 + 3H_2O \quad (16)$$

The analytical sensitivity to HClO and ClO_2^- obtained by the detection of the transient potential change in the FIA system, where a Fe(III)-Fe(II) potential buffer containing chloride was used, was enhanced by ~700-fold compared with that obtained using an equilibrium potential, as shown in Table 2. The detection limits of HClO and ClO_2^- were 5×10^{-8} M, when the potential buffer consisting of 5×10^{-4} M Fe(III) - 1×10^{-3} M Fe(II), 0.3 M KCl and 0.5 M H_2SO_4 (buffer-A) was used. For the determination of ClO_3^-, the concentration level of 10^{-5} M was detected with the use of the addition of 9 M H_2SO_4 instead of 0.5 M H_2SO_4 in buffer-A, as shown in the bottom line in Table 2.

Table 2 Sensitivities to oxychlorine species

Oxychlorine species	Sensitivity (mV/mM)		Enhancement factor
	(A) Observed in FIA	(B) Calculated	(A)/(B)
HClO	1.2×10^4	15 (n=2)	800
ClO_2^-	2.1×10^4	30 (n=4)	700
ClO_3^-	3.4	45 (n=6)	0.08
ClO_3^-	$4.3 \times 10^{2\,b}$	45 (n=6)	9.8

[a] Sensitivity calculated from Eq. (2)
[b] Slope of calibration curve observed in the FIA system with buffer-A containing 9.0 M H_2SO_4 and reaction coil (RC) of 200 cm in length
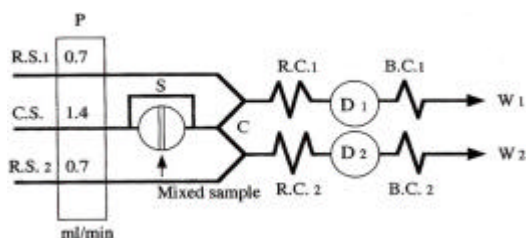

Fig.4 Schematic diagram of a three-channel FIA system for the determination of ClO_3^--ClO_2^- or ClO_3^--HClO (for the case of $[ClO_3^-] > [HClO]$ and $[ClO_3^-] > [ClO_2^-]$). R.S.$_1$, 5×10^{-3} M Fe(III)- 1×10^2 M Fe(II), 0.3 M KCl and 9 M H_2SO_4; R.S.$_2$, 5×10^{-3} M Fe(III) - 1×10^2 M Fe(II), 0.3 M KCl and 0.3 M H_2SO_4. D$_1$ and D$_2$, the same detectors as in Fig.2

A simultaneous determination of ClO_3^--ClO_2^- or ClO_3^--HClO (for the case of $[ClO_3^-] > [HClO]$ and $[ClO_3^-] > [ClO_2^-]$) was achieved by using a flow system with the dual detectors, as shown in Fig.4, where the difference in reactivity of

oxychlorine species with chloride in the potential buffer was utilized. The method was applied to the determination of residual chlorine in a tap water sample containing the large amount of chlorate. On the other hand, under the condition of $[ClO_3^-] \cong [HClO]$ and $[ClO_3^-] \cong [ClO_2^-]$, the simultaneous determination of mixed oxychlorines was conducted using a four-channel flow system equipped with a cation-exchange column in the Fe(II) form.

7. Analysis of hydrazine using a Ce(IV)-Ce(III) potential buffer [11]

The determination of trace levels of hydrazine was achieved by using an acidic Ce(IV)-Ce(III) potential buffer solution. The method is based on the measurement of a transient potential change, which appeared in a negative direction. The shape of the transient potential change observed for hydrazine was different from that observed for the determination of bromate, Cr(VI) and oxychlorine.

$$N_2H_5^+ = N_2H_4 + H^+ \quad K = 1.02 \times 10^{-8} \quad (17)$$

$$N_2H_5^+ = N_2H_3 + 2H^+ + e^- \quad E^o > -0.6\,V \quad (18)$$

$$Ce^{4+} + e^- = Ce^{3+} \ (1M\ H_2SO_4) \quad E^o = 1.44\,V \quad (19)$$

We estimated the reaction mechanism involving reactions (17), (18) and (19) in which the transient potential change was the potential shift from the Ce(IV)-Ce(III) couple to the $N_2H_5^+$-N_2 couple with a much lower electrode potential during the reaction of hydrazine with Ce(IV). The flow system was designed to detect the maximum of the transient potential change. Hydrazine, in a wide range of concentrations from 10^{-7} M to 10^{-3} M was determined by appropriately adjusting the concentration of the potential buffer from 10^{-4} M to 10^{-2} M, and the detection limit was found to be 1×10^{-7} M. The method was capable determining the hydrazine content of boiler water.

8. Conclusion

The presented method could be useful for applications to various analyses in process control and in environmental monitoring. This method involved the detection of an intermediate substance may be also applicable to the other techniques such as CFIA, batch injection and potentiometric gas sensors using a potential buffer that contains chloride or bromide.

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