Title	Rapid Determination of Iron Sulfide Content in the Sludge of Bay and Lake by Electrochemical Methods
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Citation	, .
Date of issue	2006-03
URL	http://hdl.handle.net/10173/320
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Text version	author

Rapid Determination of Iron Sulfide Content in the Sludge of Bay and Lake by Electrochemical Methods

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A dissertation submitted to
Kochi University of Technology
in partial fulfillment of the requirements
for the degree of

Doctor of Philosophy

Special Course for International Students
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March 2006

ABSTRACT

Water pollution, owing to its strong impact on the biosphere, is one of the primary concerns among the environmental problems. To remedy the polluted water resources, researchers realize that person should pay attention to sediment pollution of a water-body. Iron sulfide is an important reductive pollutant in the sediment of water-body, such as a bay and a lake. Its existence has harmful influence upon the aquatic ecosystems, so that it is essential necessary to monitor the iron sulfide content in the sediment. However, conventional chemical analysis for the determination of iron sulfide in the sludge has several disadvantages, such as tedious sampling, complicated procedure, long analysis time as well as energy-consuming.

In this thesis, we propose a new technique to determine the iron sulfide content in the sludge of bay and lake by electrochemical methods with twin-electrode, including conductometry, electrolysis and chronoamperometry. Compared with the conventional chemical method, the new technique has several advantages, such as easiness of on-site measurement, simple and rapid operation, as well as energy-saving.

Iron sulfide is slightly soluble in the water, so that it is difficult to directly determine its content by electrochemical method. However, cyclic voltammetry suggests that after electrochemically oxidation, iron sulfide can be transformed into soluble ferric ion in the sludge. This provides possibility of measurement by electrochemical method. We study the dependency of generation of ferric ion on the oxidation condition, such as oxidation potential and time of iron sulfide. It was found that oxidation potential of 2V (vs. SCE) for one minute was more suitable for the electrolysis of iron sulfide. Furthermore, when studying the correlation of iron sulfide weight percent and the concentration of ferric ion, we found a linear relationship between them. According to the linear relation, namely, the *second calibration curve* in this thesis, the iron sulfide weight percent can be evaluated from the concentration of ferric ion.

To determine the concentration of ferric ion, we proposed a novel method which can simultaneously determine the diffusion coefficient, concentration and oxidant mole fraction of reversible electrochemical active species by chronoamperometry with twin Electrode. Thus with this method, the concentration of ferric ion, which is generated

from the electrolysis of iron sulfide, can be rapidly determined by chronoamperometry with the same twin electrode as electrolysis, so that iron sulfide weight percent in the sludge can be finally evaluated by electrochemical method. Usually, the content of pollutant in the wet sludge should be evaluated by the content of pollutant in the solid component of the sludge. For determination of solid content in the sludge, dry-weight method is the routine method, but it has many shortcomings, such as long time (ca. 6 hours) and high temperature (105~110 °C) for drying, which is disadvantageous to the on-site rapid monitor of pollutant. As to this point, a novel method is proposed for the determination of solid content in the seabed sludge by conductivity measurement, namely, the *first calibration curve*.

Therefore, according to the two calibration curves, we develop a new technique to determine the iron sulfide content in the solid component of the seabed sludge by electrochemical method with twin electrode, including electrolysis, chronoamperometry and conductometry. When applying the technique to the artificial seabed sludge, we obtained a good agreement between the measured value and the reference value by preparation.

We intend to apply this technique to the determination of iron sulfide in the sludge of lake. However, the concentration of electrolyte in the lake is extremely low. This is disadvantageous to the electrochemical method. The solution to the problem is adding electrolyte to the sludge sample. We found that after adding electrolyte to the sludge sample, the first calibration curve was also applicable to the determination of solid wt% by conductometry. Moreover, adding electrolyte had little effect on the chronoamperometry itself for determining of ferric ion within the surveyed range of electrolyte level. Furthermore, it was found that the electrolysis of the iron sulfide was dependent on the concentration of electrolyte in the sludge, but usually it is difficult to evaluate the concentration of electrolyte in the sludge. Fortunately, we found that the oxidation of iron sullfide is directly proportional to the specific electrical conductivity of the disperse medium, rather than the concentration of electrolyte in the sludge, so that we can evaluate the coefficient of the second calibration curve rapidly from the conductivity of disperse medium. In this case, a method is proposed to determine the iron sulfide content in the lake sludge. When applying the method to the artificial freshwater sludge, the measured iron sulfide content agreed well with the reference

value.

However, when applying the proposed methods to the real sludge from the Uranouchi Bay and the Kasumigaura Lake, deviations were observed between the measured iron sulfide content by the proposed electrochemical method and the conventional chemical method. This is due to the existence of iron disulfide, which has different oxidation state from iron sulfide in the sludge of sea and lake. Iron disulfide responses to the electrochemical method together with iron(II) sulfide, so that the measured iron sulfide content in fact includes the total contents of iron(II) sulfide and iron disulfide, whereas the employed chemical method only measures the content of iron(II) sulfide. After considering this point, we obtained a good correlation between the two methods, suggesting that the proposed electrochemical method is reasonable to be applied to the determination of iron sulfide content in the real sludge of sea and lake. More importantly, the proposed electrochemical method makes it possible to achieve the on site measurement, which is quite useful to the protection of water environment.

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CHAPTER 1

INTRODUCTION

1.1 Research Background

With the development of society and economy, environmental problems are getting increasing attention.[1-3] Among these problems, water pollution is one of the primary concerns due to its direct effect on the aquatic ecosystem and human health.[4-6] Large amounts of industrial and domestic wastewater are discharged into the sea, river and lake, [7-10] with the growth of towns and the increasing of population. As a result, many water-bodies have been seriously polluted. Researchers gradually realize that it is necessary to concern the aquatic sediment pollution[11-14] in order to completely solve the problem of water pollution. The reason is that after biochemical process many pollutants have settled to the bottom and accumulated in the aquatic sludge. These settled pollutants will return back[15-19] into the overlying water under some condition, resulting in the secondary pollution,[20-23] such as pollution from iron sulfide. [24]

Iron sulfide is an important reductive pollutant in the aquatic sediment, [25-28] especially in the sediments of bay and lake where the water flow is poor. A number of studies suggest that the production of iron sulfide might contribute to the deterioration of water quality. For example, it is reported that iron sulfide is relevant to the occurrence of eutrophication.[29] Therefore, increasing attentions have been paid to iron sulfide in the resent years. [30-32]

1.1.1 Formation of Iron Sulfide in the Sludge of Sea and Lake[33-38]

With the human activity increasing, numerous sulphate and sulphur organic substances were discharged into the sea and lake. Via the action of anaerobic bacteria, these sulfur substances are decomposed into H_2S, HS^- and S^{2-}, which is followed by the formation of iron sulfide when ferrous ion exists (the source of ferrous ion will be introduced later). Since iron sulfide is scarcely soluble in the water, they will gradually

precipitate to the bottom and accumulate in the aquatic sludge. The sediment usually shows black color due to the existing of iron sulfide. [39]
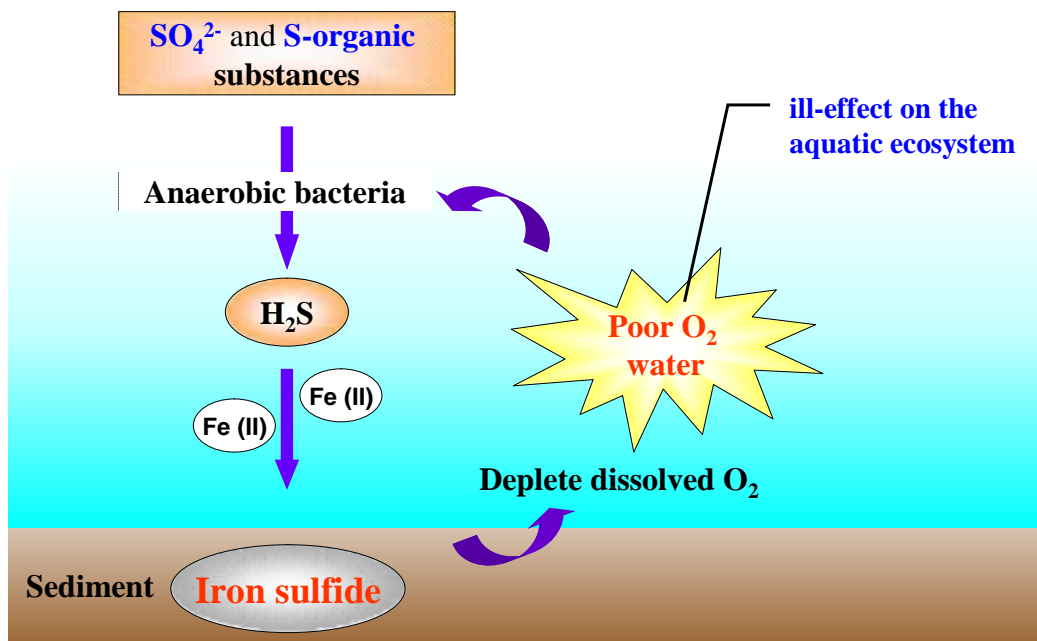
Figure 1.1 Formation of iron sulfide in the sludge of sea and lake.

1.1.2 Influence of Iron Sulfide upon the Environment

Direct Contribution to Deficiency of Dissolved Oxygen in Water. As is shown in Figure 1.1, under some conditions, such as biochemical and physical disturbance, iron sulfide in the surface sediment of sea and lake will return and dissolve into the overlying water to some degree. As a reductive substance, iron sulfide will react with dissolved oxygen, resulting in poor oxygen condition. Many aquatic organisms such as shellfish and fish will die form deficiency of oxygen. Additionally, this reductive condition will provide more favorable habitat for the anaerobic microorganism and result in much more vicious cycles. Over long-term, the aquatic ecosystem will be destroyed.

Association with Eutrophication in water-bodies. As is generally known, nitrogen species is regarded as a limiting nutrient in the coastal and lake environments. [40]

However, with increased urbanization and fertilizer use, phosphorous has become the key nutrient to the occurrence of eutrophication in water-body. When sufficient PO_4^{3-} is released from a sediment and allowed to diffuse back into the overlying water, sufficient nutrients are available for excessive plant growth (algae, periphyton attached to algae, and weeds). In this case, eutrophication takes place. [40-43] This can lead to the depletion of dissolved oxygen due to the decomposition of dead plant material, and cause other aquatic organisms to die.

It has been generally reported that there is a direct correlation between formation of iron sulfide and release of PO_4^{3-} from sediment into overlying water.[44-48] The process is relevant to the reduction of Fe(III) oxyhydroxide (FeOOH) of organic matter in freshwater and brackish sediments, as described in eq 1.1. In the sea or lake where sulfide occurs in significant concentrations, the generated Fe (II) will be subsequently removed from water by precipitation of iron sulfide that forms in the presence of H_2S (shown as eq 1.2 and Fig. 1.1).

$$424FeOOH + (CH_2O)106(NH_3)16H_3PO_4 + 756H^+$$
$$\Leftrightarrow 106HCO_3^- + 16NH_4^+ + 424Fe^{2+} + HPO_4^{2-} + 636H_2O \tag{1.1}$$

$$Fe^{2+} + HS^- \rightarrow H^+ + FeS_{aq} \rightarrow FeS_S \tag{1.2}$$
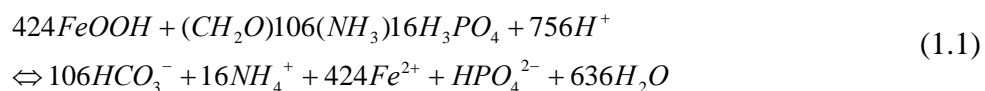
Impact on geochemical sulfur cycle. All the processes on Earth can be summarily described as material cycles. [39] From the view point of requirement of living cell, these circles can be divided into carbon cycle, hydrogen and oxygen cycles, nitrogen cycle, phosphor cycle, and sulfur cycle, as shown in Figure 1.2. These elements are the main components for the building of living cell, so whether their biogeochemical cycles can go smoothly is important for the exist of organisms on the Earth.

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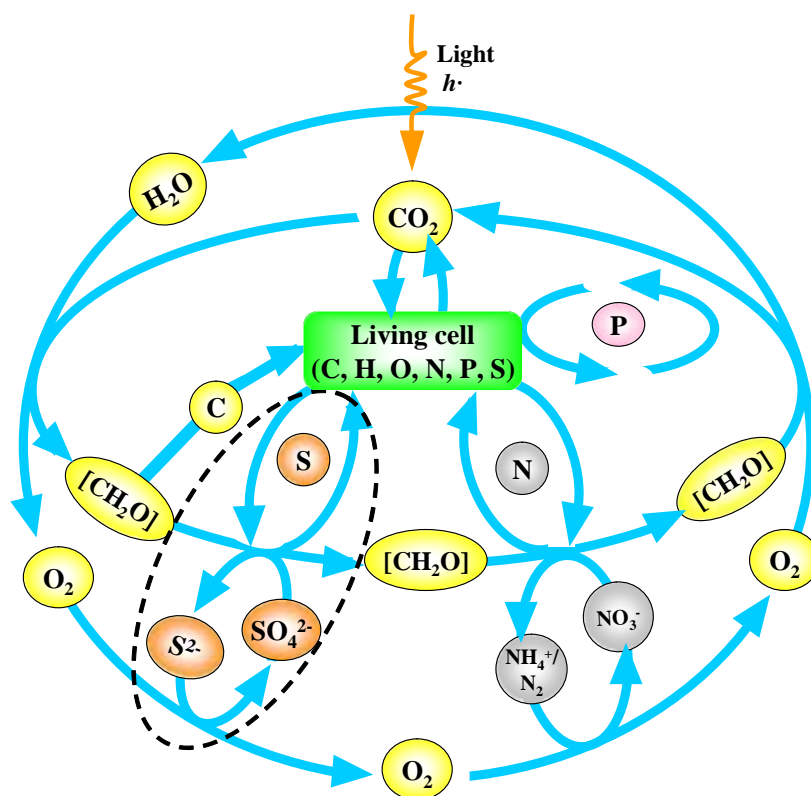
Figure 1.2 Material cycles for elements of carbon, hydrogen, oxygen, nitrogen, phosphor, and sulfur. [CH$_2$O] stands for carbohydrate.

For geochemical sulfur cycle,[49-51] there is equilibrium in the conversions of SO$_4^{2-}$ and S^{2-}. The sulfur organic substances and sulfate are reduced to hydrogen sulfide by anaerobic bacteria. Under aerobic condition, the generated hydrogen sulfide is re-oxidized to sulfate or sulfur again. In the presence of heavy metal ion, the insoluble heavy metal sulfide such as iron sulfide may form, but under aerobic condition it will be oxidized to sulfate and fed back into the cycle by chemical or biological process. In this case, there would be little iron sulfide accumulating in the sediment.

However, growing populations in the world have greatly altered the sulfur cycle. With increases in SO$_2$ emissions to atmosphere due to the combustion of sulfur-bearing fuels, and with increases in industrial and domestic wastewater discharge, too much sulfate and sulfur organic substance have come into the water-bodies. It becomes difficult to completely re-oxidize the excessive produced hydrogen sulfide or iron sulfide to sulfate. Gradually, iron sulfide will largely accumulate in the sediment. As a result, the natural sulfur cycle is destroyed.

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More important, there are intensive interactions among the cycles of different elements,[52] which can occur due to chemical and especially biochemical reactions. Therefore, over a long-term, such a change in the sulfur cycle will give considerable impact on the others.[53]

According to all the points mentioned above, iron sulfide is therefore an essentially important reductive pollutant in the aquatic sludge. It is quite necessary to monitor the content of iron sulfide in the sludge of bay and lake.

1.2 Conventional Method for the Determination of Content of Iron Sulfide in the Sludge

Usually, analytical result of pollutant content in wet sludge should be expressed on a dry basis, since water contents are variable in different sludge samples.[54] As a result, the determination of content of iron sulfide in the sludge is composed of two parts: one is evaluation of solid weight percent (wt%) in the wet sludge; the other is evaluation of iron sulfide wt% in the wet sludge.

For the evaluation of solid wt%, routine method is dry-weight determination, which is generally described as follows: weighted amount of sludge samples are dried at definite temperature (105~110 °C) to constant weight, and then solid wt% of the sludge sample is evaluated based on the ratio of mass weight after drying to that before drying. This method is not entirely satisfactory since it often requires long time (ca. 6 hours) and high temperature (105~110 °C) for drying.

For the evaluation of iron sulfide wt% in the wet sludge, traditionally utilize the chemical method for analysis of acid volatile sulfide (AVS): [55-57] after addition of acid and reducing agents to the sediment sample, the produced H_2S is distilled with N_2 to a trapping solution, which is followed by the determination of sulfide in the trapping solution through iodometric analysis. However, it has been generally reported that this chemical method has poor precision due to low trapping efficiency of sulfide. More important, the distillation of H_2S from iron sulfide after acidification always spends long time. Some researchers even recommend that 24 hours is suitable for the complete extraction of sulfide with acid. [58]

Moreover, since the measurements of both solid wt% and iron sulfide wt% require to be performed in laboratory, the whole procedures for determinations of iron sulfide content in environmental sludge had to include the processes of sampling, transportation and storage of the sludge samples.[59-60] Actually, it is tough and tedious to take sludge sample from the bottom of sea and lake. Additionally, it often requires much more attentions to prevent sludge sample from contaminating by oxidant during the process of transportation and storage.

Accordingly, the conventional method for determination of iron sulfide content in the environmental sediment has several disadvantages, such as tedious sampling, complicated procedure, long analysis time and energy-consuming (due to high temperature for drying and distillation). This makes it difficult to meet the requirement of rapid monitoring pollutant environmentally for investigating pollution state in time. In this case, it is in urgent need of developing a rapid method to determine the iron sulfide content in the sludge of sea and lake.

1.3 Overview of this Thesis

In this thesis, we propose a new technique to determine the iron sulfide content in the sludge of bay by electrochemical methods with twin-electrode, including chronoamperometry, electrolysis and conductometry. Compared with the conventional chemical method, the new technique has several advantages, such as easiness of on-line measurement, simple and rapid operation and energy-saving. After being modified, this technique can also be applied to the determination of iron sulfide content in the sludge of freshwater, such as lake. Furthermore, we will report the applicability of the proposed method to the artificial and real sludge of sea and lake for the determination of content of iron sulfide in the samples.

In Chapter 2, a new method is proposed which can simultaneously determine diffusion coefficient, concentration and oxidant mole fraction for reversible electrochemical active species by chronoamperometry in twin Electrode. For the experiment, we carried out chronoamperometry with the twin electrode in an aqueous solution including ferricyanide-ferrocyanide ion or ferrous-ferric ion. The molar fraction of the oxidant can be determined from mathematical treatment for sum of two

synchronous currents of a twin electrode (electrode 1 and electrode 2) in two potential processes. From one data of the potential processes, we can simultaneously determine the diffusion coefficient and the concentration of the species by the mathematical treatment which has not been yet reported. We carried out the potential step from E1 to E2 for electrode 1, and observed time dependence of the current of electrode 2 which was held at the potential E1. From time at the point of the extremum of a curve provided from a plot of [the current / time] vs. time, we can calculate the diffusion coefficient of the species. Furthermore, from the diffusion coefficient of the species and the extremum of the curve, we can calculate the concentration of the species. Even if the diffusion coefficient of the species in the solution such as environmental sample, is unknown, we can determine the concentration of the species by this method because the diffusion coefficient can be evaluated in every sample. This study provides the theoretical base for the determination of ferric/ferrous ion form the electrolysis of iron sulfide in the sludge by electrochemical method with twin electrode, which will be introduced in later chapters.

In Chapter 3, a behavior of conductivity *vs.* solid fractional volume was investigated in various suspensions. We found a linear relation between the conductivity ratio and the solid fractional volume in the suspensions within the surveyed range. On the basis of this linear relation, an empirical equation is proposed by $\kappa/\kappa_0 = 1 - 1.79 V_f \, (0 \le V_f < ca.0.25)$, where κ and κ_0 are the specific conductivity of the suspension and the disperse medium, respectively, and V_f is the solid fractional volume in the suspension. According to the proposed empirical equation, we can determine the solid fractional volume, V_f, in the suspension by conductivity measurement. From the value of V_f, we can readily evaluate solid weight percent in the suspension with the density of dry dispersoid. Actually, in this thesis, the empirical equation is also called "*the fist calibration curve*" which is used to determine the solid weight percent in the suspension sample. When applying the conductivity method to the seabed sludge samples, we obtained a good agreement between the measured results by conventional dry-weight method and the proposed conductivity method. Moreover, a theoretical consideration was given to the conductivity method by a comparison of the empirical equation with Maxwell-Wagner model. A good agreement was obtained between the

curve from the empirical equation and that from the Maxwell-Wagner model. Furthermore, the behaviors of conductive dispersoids in the suspension were discussed.

In chapter 4, a new electrochemical method with twin electrode was proposed to determine the iron sulfide content in the seabed sludge. Iron sulfide is slightly soluble in the water, so that it is difficult to directly determine the iron sulfide content by electrochemical method. However, cyclic voltammetry suggested that after electrochemically oxidation by twin electrode, the iron sulfide in the sludge can be transformed into soluble ferric ion. This provides possibility of being measured by electrochemical method. We investigated the influence of oxidation condition, such as oxidation potential and oxidation time, on the generation of ferric ion. Additionally, the correlation was studied between the iron sulfide weight percent and the concentration of ferric ion generated in the sludge. We found a linear relation between them, namely *the second calibration cure*, according to which, the iron sulfide weight percent can be evaluated from the concentration of ferric ion. The technique of chronoamperometry with twin electrode, which had been introduced in Chapter 2, was employed to determine the concentration of ferric ion. On the other hand, the conductometry which was proposed in Chapter 3 was used to determine the solid weight in the sludge, so that finally the iron sulfide content in the solid component of sludge can be determined by a new electrochemical technology with twin electrode. Moreover, to validate the feasibility of the new technique, it has been applied to the artificial and real seedbed sludge. Furthermore, we discussed the deviation between the electrochemical method and the conventional chemical method for the determination of iron sulfide content in the real seabed sludge from Uranouchi Bay.

In Chapter 5, the proposed technique which is suitable to the seabed sludge sample was modified to determine the content of iron sulfide in the sludge of lake. However, the concentration of electrolyte in the lake is extremely low. This is disadvantageous to the flow of electric current which is necessary for an electrochemical method. The solution to the problem is addition of electrolyte to the sludge, but after addition of electrolyte, the concentration of electrolyte in the sludge sample will be changed. It was found that the first calibration equation is independent of the concentration of electrolyte, while the second one changes with the concentration of the electrolyte. We investigated the coefficient of the slope of the second calibration curve for various

sludge samples with different concentration of the electrolyte. As a result, this coefficient is proportional to the specific electric conductivity of the disperse medium, κ_0, rather than the concentration of electrolyte. Based on this result, we proposed a method for the evaluation of iron sulfide content in the sludge of lake. When applying this method to the artificial and real sludge of freshwater, we observed good agreements between the measured results and the reference values. In addition, we evaluated the applicability of the technique with only twin electrode for the determination of iron sulfide in the freshwater sludge sample. This will be quite useful to the achievement of on site measurement of the pollutant in the sludge of environment.

Chapter 6 described conclusions of this thesis. Moreover, some advices were given to the future research.

CHAPTER 2

RAPID DETERMINATION OF ELECTROACTIVE SPECIES BY CHRONOAMPEROMETRY IN TWIN ELECTRODE

2.1 Introduction

In chemical analysis of environment, on-site measurements are important from the viewpoints of shortening of sample collection and regular observation. An electrochemical analysis is a simple, easy and effective method in the on-site measurements. Therefore, the electrochemical analytical methods have been used as abbreviated analysis equipment of examination of water. There are potentiometry and voltammetry when we classify electrochemical analysis in two categories, and we use these methods depending on purpose complementarily.

The potentiometry is a simple and easy method, but needs a calibration curve. Potentiometry is subject to be often influenced by interfering ion, and it is necessary for composition of a measurement object to be clear. When we analyze samples in environment by the potentiometry on-site, we always have an uncertain factor that the samples include the interfering ion to assay ion.

In voltammetry, we can analyze electrochemically active species. For example, square wave voltammetry or stripping voltammetry have high sensitivity for the determination of concentration of the species.[61, 62, 63] Especially, the stripping voltammetry has an unique technique which concentrate the species on the electrode by electrode reaction and then analyze them. Therefore, in the voltammetry, we can analyze the species after electrode reaction even if we cannot directly analyze them in potentiometry. In that case, the voltammetry is more useful than the potentiometry.

In general, the voltammetry also needs calibration curve about quantitative analysis. [64, 65] When analyze the environmental samples by the voltammetry, we must use the calibration curve. This includes the condition that the diffusion coefficient of species in the environmental samples must be the same as that in the solution prepared for the

calibration curve. However, the diffusion coefficient of the species in each environmental sample may be different from that in the prepared samples at the laboratory. If we do not know the diffusion coefficient of the species in the environmental samples, it becomes difficult to determine the concentration of the species by the standard electrochemical methods such as chronoamperometry and chronocoulometry without calibration curves. Therefore, it is very important that we determine the diffusion coefficient and the concentration of the species for each sample simultaneously.

One of the techniques for the simultaneous measurement is the hydrodynamic chronocoulometry using the rotating disk electrode. [66, 67] The diffusion coefficient and the concentration of $Fe(CN)_6^{3-/4-}$ ion can be simultaneously determined by this technique even if both values are unknown. Though this is an excellent method, they must predetermine the kinetic viscosity of the sample solutions to estimate the concentration and the diffusion coefficient from data of the hydrodynamic chronocoulometry. If the kinetic viscosity of each sample solution such as environmental sample is different, we cannot estimate the concentration of the species because of the change of the kinetic viscosity. This means that there may be an uncertain factor for the estimation of the concentration of the species by the hydrodynamic chronocoulometry in the environmental samples. Electrochemical technique with microdisk electrode also enables an estimate of diffusion coefficient and concentration of species. This technique principally enabled assay in microscopic domain and developed to scanning electrochemical microscope.[68,69] In the research process, a direct determination method of diffusion coefficient of species have been reported by a chronoamperometry in microdisk electrode[70], and this technology enables simultaneous determination of diffusion coefficient and concentration.[71,72, 73]

In this study, we carried out a chronoamperometry by a twin electrode in the aqueous solution with electrochemical active species such as $Fe(CN)_6^{4-/3-}$ and $Fe^{3+/2+}$ to estimate the diffusion coefficient and the concentration of the species simultaneously. Electrochemistry with the twin electrode belongs to the field of thin-layer electrochemistry. The thin-layer electrochemistry was first studied in the early1960's, and potential step methods and potential sweep methods were studied.[74, 75, 76] S. J. Konopka and B. McDuffie reported that they could determine the diffusion coefficient

of species through measurement of coulometry and chronoamperometry.[77,78] Therefore, fundamentally the chronoamperometry with the twin electrode can estimate the diffusion coefficient and the concentration of species simultaneously. From this point of view, we show that the diffusion coefficient, the concentration and the molar fraction of the oxidant can be determined simultaneously by the mathematical treatment which is not yet reported. The characteristic with the twin electrode is that the domain of electrode reaction is limited in the space between two electrodes. Therefore, we can measure the concentration of the species which is produced by electrode reaction in the limited domain even if it is heterogeneous system such as suspension. For the environmental suspension, we can analyze the species produced after the electrode reaction with the twin electrode. In such the case, because the diffusion coefficient of the species is unknown, it is important to determine the diffusion coefficient and the concentration simultaneously. In Chapter 4, we will report about electrochemical techniques by which we can directly analyze the suspension such as sludge in the environmental samples with the twin electrode. [79, 80]

2.2 Experimental Section

2.2.1 Twin Electrode

Two platinum plates were purchased from Nilaco Co., were cut as shown in Figure 2.1 and were separated by a Teflon spacer with thickness of 300μm to compose a twin electrode. The twin electrode has an effective area of 4cm^2 and a clearance of 300μm. The twin electrode was assembled in a holder. We immersed the whole electrode with the holder in the sample solution to make experiments on the chronoamperometry.
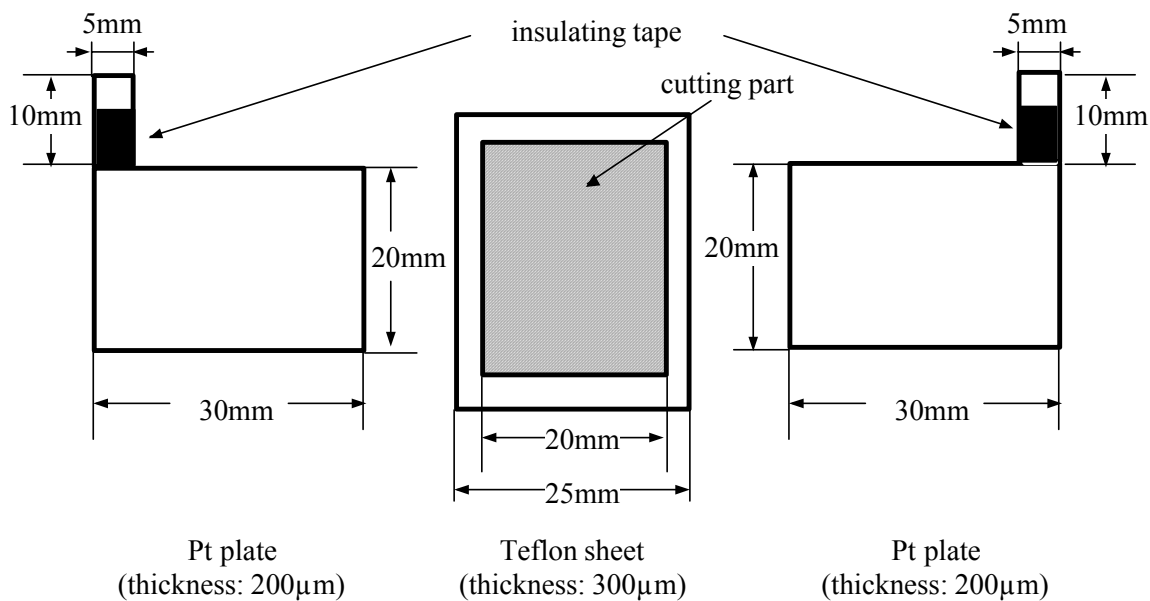
Figure 2.1 Structure of twin electrode. The twin electrode is assembled by superposition of a Pt plate, a Teflon spacer and another Pt plate in a cell holder.

2.2.2 Reagents and Supporting Electrolyte Solutions

Ferrocyanide-ferricyanide and ferrous-ferric ions are used as redox couples. The reagents, $K_4Fe(CN)_6$ $3H_2O$, $K_3Fe(CN)_6$, $(NH_4)_2Fe(SO_4)_2$ $6H_2O$ and $NH_4Fe(SO_4)_2$ $12H_2O$ were purchased from Nacalai Tesque. For the preparation of $Fe(CN)_6^{3-/4-}$ solutions, 0.5 M NaCl aqueous solution was used as a supporting electrolyte solution, and for the preparation of $Fe^{3-/4-}$ solution, 0.2M HCl-KCl buffer solution of pH 2.0 was used.

2.2.3 Equipments

Dual Potentiostat, BAS Co., was used for chronoamperometry in the twin electrode system. The currents of the working electrode 1 and 2 are recorded with Digital recorder, Yokogawa, DL708.

2.2.4 Chronoamperometry with Twin Electrode

To obtain the diffusion coefficient, concentration and oxidant mole fraction, the following types of chronoamperometry were carried out with the twin electrode for the solutions of $Fe(CN)_6^{3-/4-}$ or $Fe^{3+/2+}$.

i) Potential process A

Both electrodes are on stand-by before time is the zero second. At the zero second of time, the potential E_1 is applied on the electrode 1, and the potential E_2 on the electrode 2 ($E_1 < E_2$). The potentials E_1 and E_2 are kept after zero second of time. On the electrode 1 with the potential E_1, almost 100% of the electrochemically active species exists as the reductant, and on the electrode 2 with the potential E_2 as the oxidant. For the solution of $Fe(CN)_6^{3-/4-}$, E_1 is $0V$ (*vs.* SCE), and E_2 is $+0.4V$; for the solution of $Fe^{3+/2+}$, E_1 is $+0.3V$ and E_2 is $+0.7V$. The currents on both electrodes are recorded with digital recorder.

ii) Potential process B

Potential E_2 are applied on the both electrodes before time is the zero second. At the zero second of time, the potential of the electrode 1 is stepped from E_2 to E_1, and the potential of the electrode 2 is kept at E_2. The potentials are kept after the potential step. For the solution of $Fe(CN)_6^{3-/4-}$, E_1 is $0V$ (*vs.* SCE) and E_2 is $+0.4V$.

iii) Potential process C

Potential E_1 is applied on the electrode 1 and E_2 is on the electrode 2 before time is the zero second. At the zero second of time, the potential of the electrode 1 is stepped from E_1 to E_2, and the potential of the electrode 2 is kept at E_2. The potential is kept after the potential step. For the solution of $Fe^{3+/2+}$, E_1 is $+0.3V$ (*vs.* SCE) and E_2 is $+0.7V$. The currents on both electrodes are recorded with digital recorder.

2.3 Theoretical Basis

In the processes A, B and C, we represent the observed currents on the electrode 1 and 2 as i_{A1}, i_{A2}, i_{B1}, i_{B2}, i_{C1} and i_{C2}, respectively. We can theoretically obtain these currents from a diffusion equation in the twin electrode with area A and distance L. We obtain the following solution for the diffusion equation which has been already resolved by the heat diffusion theory.[81]

$$C_O(x,t) = c_{E1} + (c_{E2} - c_{E1})\frac{x}{L} + \frac{2}{\pi}\sum_{1}^{\infty}\frac{c_{E2}\cos n\pi - c_{E1}}{n}\sin\frac{n\pi x}{L}F(t)$$
$$+\frac{2}{L}\sum_{1}^{\infty}\sin\frac{n\pi x}{L}F(t)\int_{0}^{l}f(x')\sin\frac{n\pi x'}{L}dx' \tag{2.1}$$

where $F(t)$ is given by the following equation.

$$F(t) = \exp\left(\frac{-Dn^2\pi^2 t}{L^2}\right) \tag{2.2}$$

In eq 2.1, $C_O(x, t)$ is the oxidant concentration on the position x ($0 < x < L$) at a time t. The concentrations, c_{E1} and c_{E2}, are oxidant concentration on the electrode 1 and 2 after zero second, respectively. The function, f(x'), shows the concentration profile before time zero. In eq 2.2, D is the diffusion coefficient of the redox species.

For the process A, the boundary conditions are shown as following:

$$c_{E1} = 0, \ c_{E2} = C_{OR} \qquad (t \geq 0) \tag{2.3}$$

$$f(x') = C_O(x, 0) = \chi_0 \, C_{OR} \qquad (t < 0) \tag{2.4}$$

where C_{OR} is total concentration of the oxidant and the reductant, and χ_0 is mole fraction of the oxidant. Because theoretical currents are given by eqs 2.5 and 2.6:

$$\frac{i_{A1}}{nFA} = D_O\left[\frac{\partial C_O(x,t)}{\partial x}\right]_{x=0} \tag{2.5}$$

$$\frac{i_{A2}}{nFA} = -D_O\left[\frac{\partial C_O(x,t)}{\partial x}\right]_{x=L} \tag{2.6}$$

We can get the following equations:

$$i_{A1}\left(\frac{L}{nFADC_{OR}}\right) = 1 + 2\sum_{1}^{\infty}\left[(1 - \chi_O)\cos n\pi + \chi_O\right]F(t) \tag{2.7}$$

$$i_{A2}\left(\frac{L}{nFADC_{OR}}\right) = -1 - 2\sum_{1}^{\infty}\left[1 - \chi_O + \chi_O\cos n\pi\right]\cdot F(t) \tag{2.8}$$

where F is the Faraday's constant and n is electron number related with electrode reaction. A sum of two synchronous currents of the electrode 1 and 2, I_A, is given by a sum of eqs 2.7 and 2.8.

$$I_A\left(\frac{L}{nFADC_{OR}}\right) = 2(1 - 2\chi_O)\sum_{1}^{\infty}(\cos n\pi - 1)F(t) \tag{2.9}$$

It is an important point that χ_o inside of the summation function Σ in eqs 2.7 and 2.8 is outside of the summation in eq 2.9.

For the process B, the boundary condition is shown as following:

$$c_{E1} = 0, \ c_{E2} = C_{OR} \qquad (t \geq 0) \tag{2.10}$$

$$C_O(x, 0) = C_{OR} \qquad (t < 0) \tag{2.11}$$

This boundary condition is the same condition as the case that the mole fraction of oxidant is equal to unity in the process A ($\chi_o = 1$). Therefore, we can easily get eqs 2.12 and 2.13 from eqs 2.7 and 2.8.

$$i_{B1}\left(\frac{L}{nFADC_{OR}}\right) = 1 + 2\sum_{1}^{\infty}F(t) \tag{2.12}$$

$$i_{B2}\left(\frac{L}{nFADC_{OR}}\right) = -1 - 2\sum_{1}^{\infty}\cos n\pi\cdot F(t) \tag{2.13}$$

A sum of two synchronous currents of the electrode 1 and 2, I_B ($I_B=i_{B1}+i_{B2}$), is given by a sum of eqs 2.12 and 2.13.

$$I_B \left(\frac{L}{nFADC_{OR}} \right) = -2 \sum_1^\infty (\cos n\pi - 1) F(t) \qquad (2.14)$$

We can obtain the following relation by eliminating the summation function Σ in eqs 2.9 and 2.15:

$$I_A = (2\chi_O - 1) I_B \qquad (2.15)$$

For the process C, the boundary condition is shown as following:

$$c_{E1} = C_{OR}, \ c_{E2} = C_{OR} \qquad (t \geq 0) \qquad (2.16)$$

$$C_O(x,0) = \frac{C_{OR}}{L} x \qquad (t < 0) \qquad (2.17)$$

From this boundary condition, we get theoretical equations, 2.18 and 2.19, which correspond with eqs 2.12 and 2.13:

$$i_{C1} \left(\frac{L}{nFADC_{OR}} \right) = -2 \sum_1^\infty F(t) \qquad (2.18)$$

$$i_{C2} \left(\frac{L}{nFADC_{OR}} \right) = 2 \sum_1^\infty \cos n\pi \cdot F(t) \qquad (2.19)$$

A sum of two synchronous currents of the electrode 1 and 2, I_C ($I_C=i_{C1}+i_{C2}$), is given by a sum of eqs 2.12 and 2.13.

$$I_C \left(\frac{L}{nFADC_{OR}} \right) = 2 \sum_1^\infty (\cos n\pi - 1) F(t) \qquad (2.20)$$

We can obtain the following relation by eliminating the summation function Σ in eqs 2.9 and 2.20:

$$I_A = \left(1 - 2\chi_O\right)I_C \tag{2.21}$$

2.4 Results and Discussion

2.4.1 Determination of oxidant mole fraction

The eq 2.15 predicts that the current summation for the process A has a linear relationship with that for the process B. The slope of the straight line is equal to $2\chi_o - 1$. To confirm this relationship, we carried out the potential processes, A and B for the aqueous solutions of $Fe(CN)_6^{3-/4-}$. We prepared eleven sample solutions with different oxidant mole fractions from zero to 1.0 at intervals of 0.1, in which the total concentrations of redox species are the same (1mM).

As an example, we show the time-current curves of the electrode 1 and 2 for a sample solution with 0.70 mM of ferricyanide and 0.30 mM of ferrocyanide in Figure 2.2. The currents i_{A1}, i_{A2} and i_{B1} decrease monotonously. However, the current, i_{B2} shows a sigmoid curve that corresponds with the theoretical curve of eq 2.13. We obtain the value I_A from the sum of i_{A1} and i_{A2} in Figure 2.2A (a and b), and the value I_B from the sum of i_{B1} and i_{B2} in Figure 2.2B (c and d).
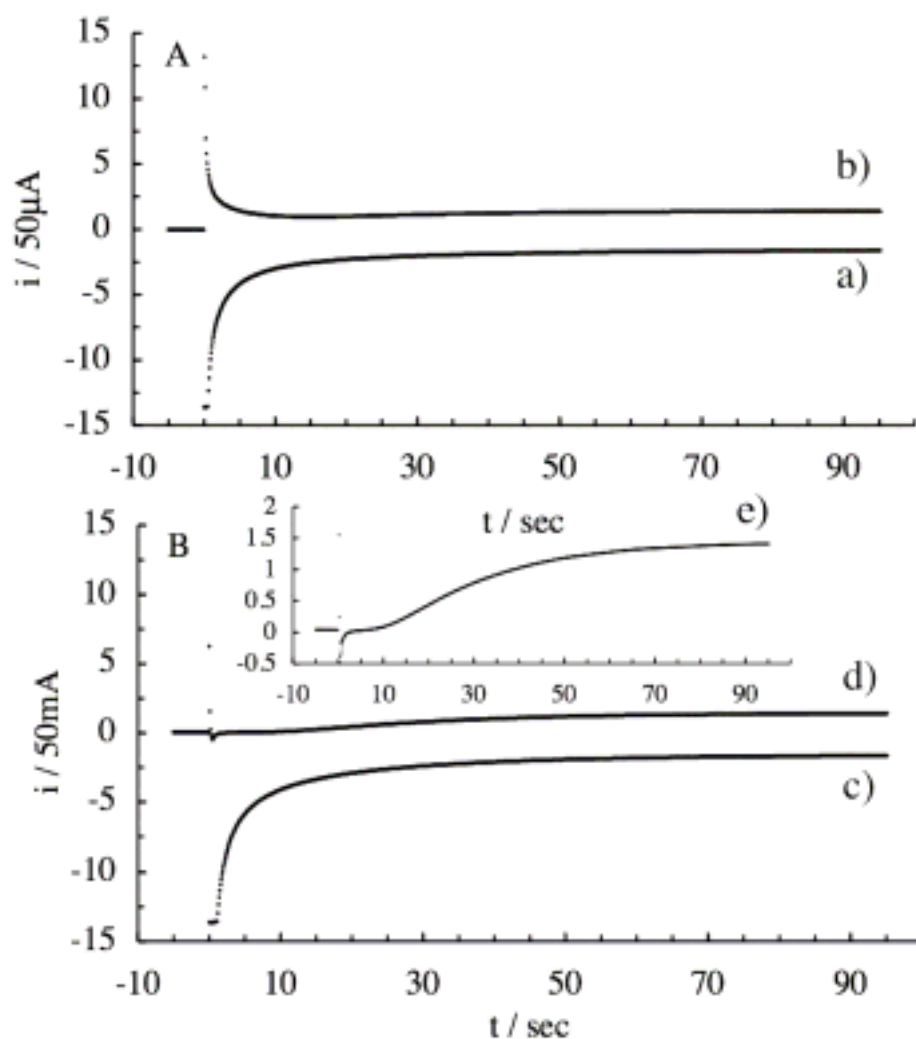
Figure 2.2 Current responses of chronoamperometry in the twin electrode. Response a): electrode 1, b): electrode 2 in the process A, and c): electrode 1, d): electrode 2 in the process B. Response e) is the enlarged figure of the response d).

The relations between I_A and I_B are shown in Figure 2.3 for the five kinds of solution with the different oxidant mole fraction, in which the total concentration of $Fe(CN)_6^{3-/4-}$ is 1mM. The all plots show the data for the period from 8 sec. to 40 sec. in the process A and B. They certainly give good linear relations. We can calculate the oxidant mole fractions from the linear slopes because the slopes equal to $(2\chi_o - 1)$. As for 0.70 of the mole fraction, the linear slope is 0.45 (Figure 2.3 d). From the equation, $2\chi_o - 1 = 0.45$,

we can estimate that the oxidant mole fraction is 0.72. This value agrees with 0.70 of the prepared mole fraction. For the samples with χ_o of the oxidant mole fraction, we can estimate the mole fraction, χ_{tw}, by the linear slopes of relation between I_A and I_B, where the subscripts "tw" means twin electrode. A plot of χ_{tw} vs. χ_o is shown in Figure 2.4a. The values χ_{tw} obviously agree with the values χ_o.

Therefore, we can determine the oxidant mole fractions through the chronoamperometry in the twin electrode system. If the sample does not contain any other redox species with the redox potential between E_1 and E_2, this method can be applied to the sample. If the sample has other redox species with larger redox potential than E_2 or with smaller redox potential than E_1, we can discuss the following. If the sample has other oxidants which completely oxidize $Fe(CN)_6^{4-}$, the value I_A/I_B will be always larger than 1. In this case, the value, χ_{tw} should be 1. If the sample has other reductants which completely reduce $Fe(CN)_6^{3-}$, the value I_A/I_B will be always smaller than -1. In this case, the value χ_{tw} should be zero.

The eq 2.21 predicts that the current summation for Chronoamperometry A, I_A, has a linear relationship with that for Chronoamperometry C, I_C, and that the linear slope equals to $(2\chi_o-1)$. To confirm this relationship, we carried out Chronoamperometry A and C for the solutions of $Fe^{3+/2+}$. For Chronoamperometry A and C, we got the similar results to the experiment of Chronoamperometry A and B for $Fe(CN)_6^{3-/4-}$, as shown in Figure 2.3b and Figure 2.4b.
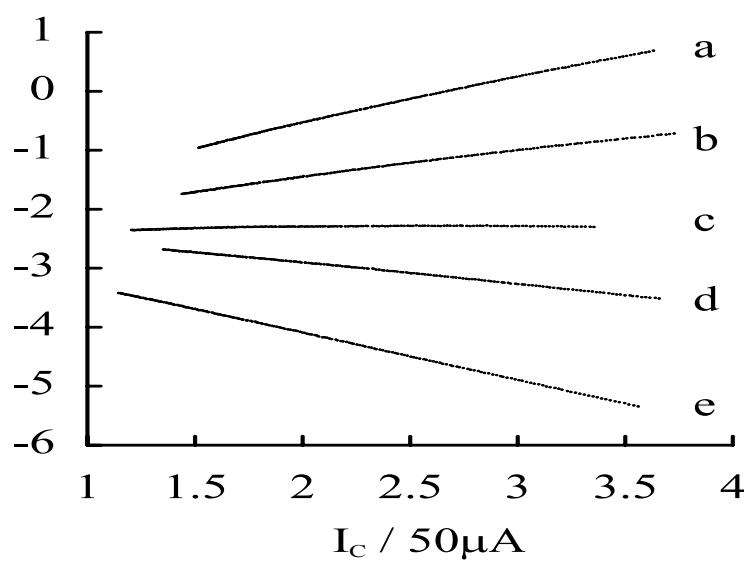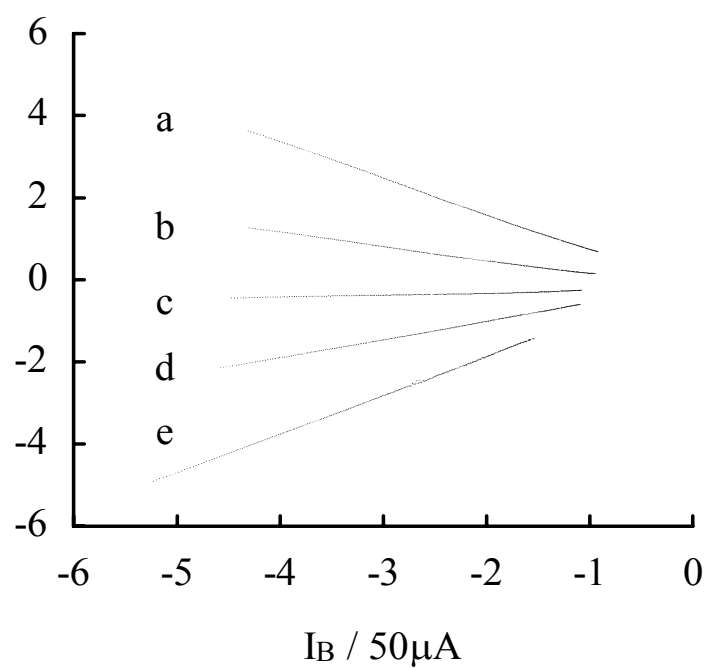
Figure 2.3 Plots of I_A *vs.* I_B (left) and of I_A *vs.* I_C (right). Data points are shown with closed circle (•) in the figures. Oxidant mole fraction, a: 0, b: 0.3, c: 0.5, d: 0.7, e: 1.0

a

b
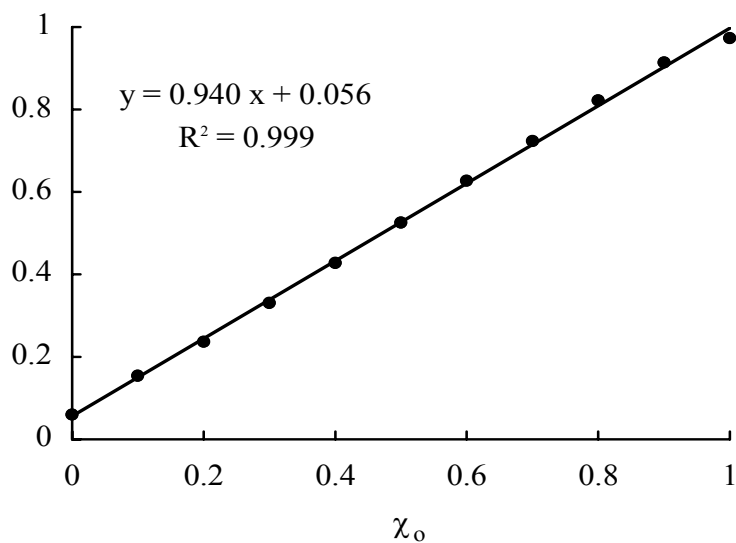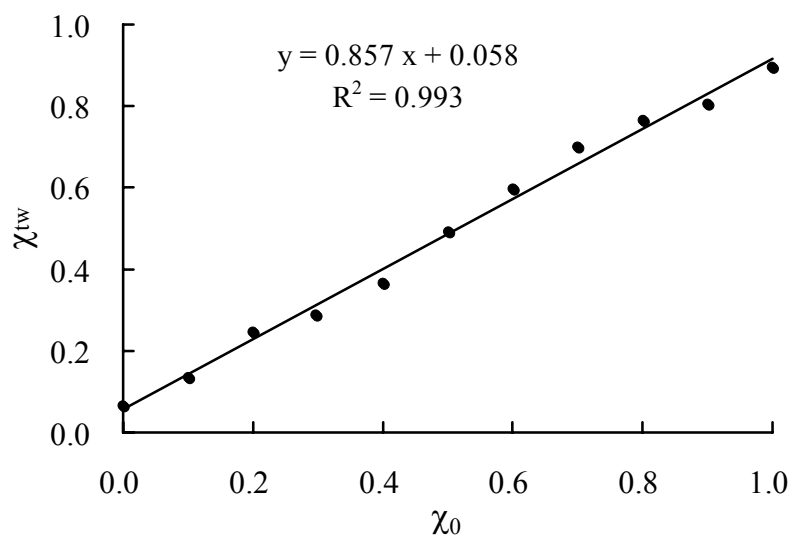
Figure 2.4 Plot of χ_{tw} vs. χ_o, where χ_{tw} is calculated from the slopes of the straight line in the plot of I_A *vs.* I_B such as Figure 2.3, and χ_o is the adjusted oxidant mole fraction. a: $Fe(CN)_6^{3-/4-}$ (χ_{tw} is given by eq 2.15), b: $Fe^{3+/2+}$ (χ_{tw} is given by eq 2.20).

2.4.2 Determination of Diffusion Coefficient and Concentration
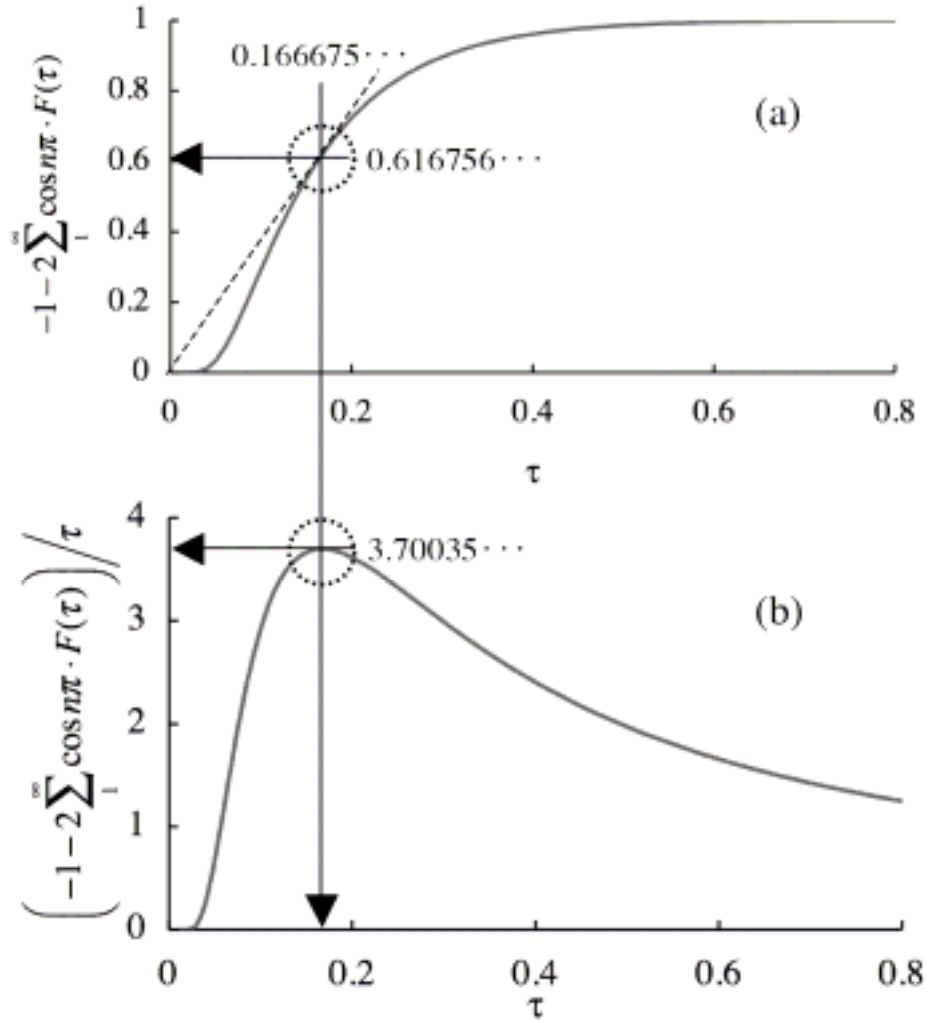
Figure 2.5 Theoretical curves of eq 2.13(a) and eq 2.22(b). The values τ_{ext}, r_{ext} and τ_{ext} r_{extr} are given in the figures.

We can determine the diffusion coefficient and the concentration of the oxidant simultaneously by using eq 2.13. The theoretical curve of eq 2.13 is shown in Figure 2.5a, where $\tau = (D/L^2)t$. Basically, it is possible to determine the diffusion coefficient and the concentration by a curve fitting method to the current i_{B2}-time curve as shown in

Figure 2.2B (e) to the theoretical curve. However, this method is a taxing way because eq 2.13 is quite complex. Other methods that we can estimate them easily are to read the following values for current and time:

i) Current and time at inflection point in the sigmoid curve as shown in Figure 2.2B (e) ($i_{B2, inf}$, t_{inf})

ii) Limiting current and the time at half of the limiting current ($i_{B2, lim}$, $t_{1/2}$)

iii) Current and time at an extremum of the curve for [current/time] vs. time ($i_{B2, ext}$, t_{ext})

For the method i), the inflection point has the condition that the value of the twice differential of eq 2.13 by τ equals 0 as the following equation. We can find a value $\tau_{inf} = 0.09175171$, which satisfies eq 2.16.

$$\frac{d^2 i_{B2}}{d\tau^2}\left(\frac{L}{nFADC_{OR}}\right) = -2\sum_{1}^{\infty}(n\pi)^4 \cos n\pi F(\tau) = 0 \qquad (2.16)$$

Therefore, we can represent the current and the time at the inflection point as the following equations eqs 2.17 and 2.18.

$$i_{B2}\left(\frac{L}{nFADC_{OR}}\right) = 0.244234111\cdots \qquad (2.17)$$

$$\tau_{inf} = \left(\frac{D}{L^2}\right)t_{inf} = 0.09175171\cdots \qquad (2.18)$$

For the method ii), the limiting current is represented as the following equations by eq 2.19.

$$i_{B2,lim} = -nFAD\left(\frac{L}{C_{OR}}\right) \qquad (2.19)$$

The time $\tau_{1/2}$ at half of the limiting current satisfies the following equations.

24

$$i_{B2}\left(\frac{L}{nFADC_{OR}}\right) = -1 - 2\sum \cos n\pi \cdot F\left(\tau_{1/2}\right) = 0.5 \tag{2.20}$$

$$\tau_{1/2} = \left(\frac{D}{L^2}\right)t_{1/2} = 0.1387852\cdots\cdots \tag{2.21}$$

For the method iii), we take a function r_{B2}, which is given by dividing current i_{B2} by time τ, as shown in eq 2.22.

$$r_{B2} = \left(\frac{i_{B2}}{\tau}\right)\left(\frac{L}{nFADC_{OR}}\right) = \frac{\left(-1 - 2\sum \cos n\pi \cdot F(\tau)\right)}{\tau} \tag{2.22}$$

Theoretical curve for eq 2.22 that is shown in Figure 2.5b, has an extremum. The extremum, $r_{B2,\,ext}$ is 3.70035 . At the extremum, the values τ_{ext} and $r_{B2,\,ext} \cdot \tau_{ext}$ are 0.166675$\cdots$ and 0.616756$\cdots$, respectively, and related with the time t_{ext} and the current $i_{B2,max}$ at the extremum in the observed curve, as shown in eqs 2.23 and 2.24.

$$\tau_{ext} = \left(\frac{D}{L^2}\right)t_{ext} = 0.166675\cdots\cdots \tag{2.23}$$

$$r_{B2,\,ext} \cdot \tau_{B2,\,ext} = i_{B2,\,ext}\left(\frac{L}{nFADC_{OR}}\right) = 0.616756..... \tag{2.24}$$

The method i) is elegant method. However, if the current data has often noise, it will be difficult to treat the data because differential processes increase the noise. Furthermore, because the time at the inflection point is shortest in the three methods, a large noise by potential step is liable to overlap the faradic current. This will derange the inflection point.

The method ii) is easy and relatively reliable as an idea. However, if the distance between two electrodes is relatively long or the value of diffusion coefficient is

relatively small, it will take long time to get the limiting current. We have often experience that the limiting current that should be flat, gradually decreases, probably because of inactivation of electrode surface. In this case, we underestimate the limiting current and half of limiting current, and then overestimate the diffusion coefficient.

The method iii) has both advantages of the methods i) and ii). The point at an extremum of the curve for [current/time] vs. time corresponds to a point of contact in the tangent from origin to the sigmoid curve. We can easily read the point because the division of current by time does not amplify the noise in the current. We can easily know the end of measurement differently to method ii). Furthermore, the point is not liable to be disturbed by the large noise arising from potential step because the time, τ_{ext}, is larger than τ_{inf} and $\tau_{1/2}$. Therefore, we select the method iii) for analysis of the current-time curve.
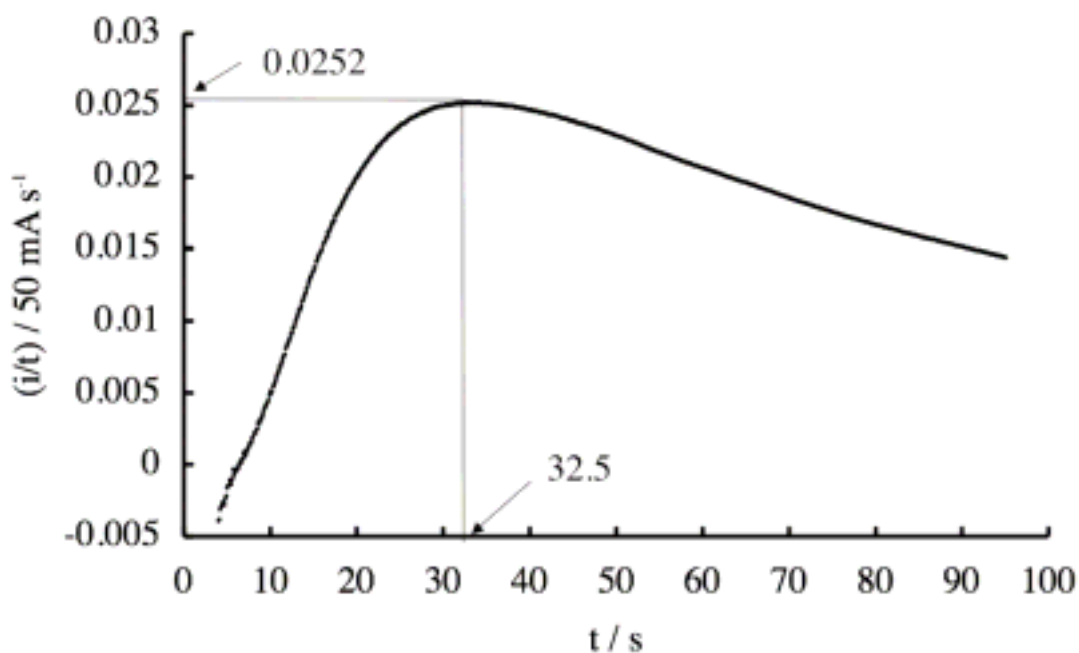
Figure 2.6 A plot of [current/time] *vs.* time for the curve in Figure 2.2e. The numbers of arrows show the x and y axial values at the extremum.

In the experiment, we measure the time-current curve for i_{B2} such as Figure 2.2e, make a curve by a plot of [current/time] *vs.* time and read the time t_{ext} and the current $i_{B2, ext}$ at a extremum of the curve. From eq 2.23 and the time t_{ext}, we can evaluate the diffusion coefficient of the electrochemically active species in the sample solution. Finally, we can determine the concentration of the species from eq 2.24, the diffusion coefficient and the current $i_{B2, ext}$. As an example, we have shown the time-current curve for i_{B2} in the solution with 0.70 mM of ferricyanide and 0.30 mM of ferrocyanide in Figure 2.2e. A plot of [current/time] *vs.* time from this curve is shown in Figure 2.6. The plot shows the curve with an extremum value at 32.5 sec. In the eq 2.23, we obtain the apparent diffusion coefficient of $Fe(CN)_6^{3-/4-}$, $D_{app} = 4.62 \times 10^{-6}$ cm^2 sec^{-1}, where L = 0.0300 cm. As the y axial value at the extremum is 0.0252 × 50 mA sec^{-1}, we can read the current at extremum, $i_{B2, ext}$, as 41.0 µA and estimate the concentration of $Fe(CN)_6^{3-/4-}$, C_{tw}, with 1.12 mM. We can regard that this value almost agrees with 1.00 mM of the concentration of the solution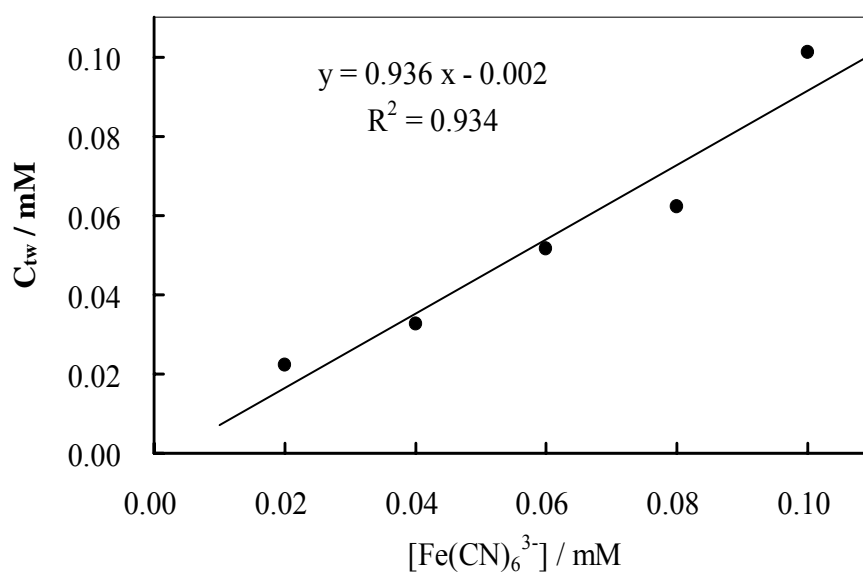 which we prepared, when we consider the fact that we do not compensate at all. Figure 2.7 shows the relationship of the concentration of $Fe(CN)_6^{3-}$, C_{tw}, which was estimated from electrochemical data and eq 2.24, and the concentration of $Fe(CN)_6^{3-}$, $[Fe(CN)_6^{3-}]$. We confirmed that this method is effective more than about 0.02 mM. For the higher concentration, the limitation depends on the performance of potentiostat. For the lower concentration, the limitation is substantial. We have to decide the current position at time zero. When we apply the potential step of electrode 1 from E_2 to E_1, the current of electrode 2 deviates a little before and after the potential step. Deviation of the current is not constant and within about 0.17 µA, corresponding with about 5 µM of the concentration of $Fe(CN)_6^{3-}$ or Fe^{3+}. This means that the concentration C_{tw} has an absolute error of about 5 µM.

a

$$y = 1.154\ x - 0.027$$
$$R^2 = 0.999$$

C_{tw} / mM

$[Fe(CN)_6]^{3-} / mM$

b

$$y = 0.936\ x - 0.002$$
$$R^2 = 0.934$$

C_{tw} / mM
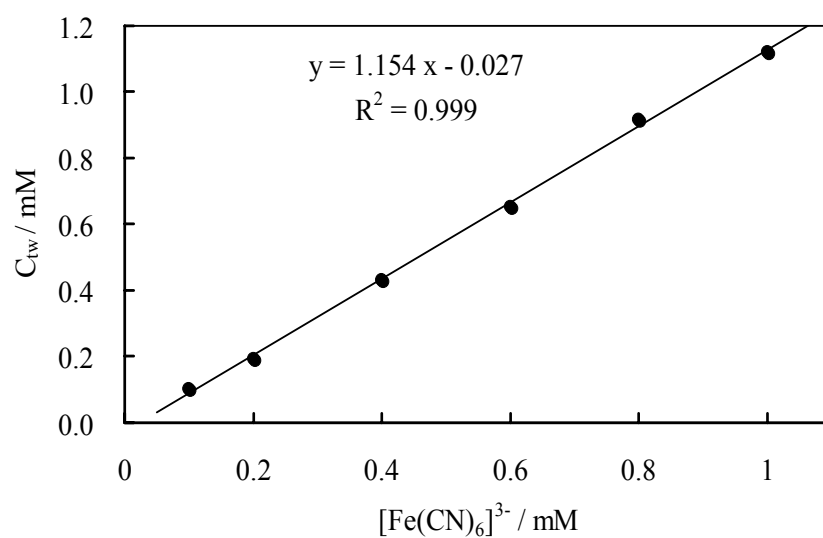
$[Fe(CN)_6^{3-}] / mM$

Figure 2.7 Relationship of the concentration estimated from measurement data and eq 2.24, C_{tw}, and the concentration prepared, $[Fe(CN)_6^{3-}]$. a: $[Fe(CN)_6^{3-}] = 0$-1 mM; b: $[Fe(CN)_6^{3-}] = 0$-0.1 mM.

2.5 Conclusions

We applied the chronoamperometry with the twin electrode and found that we can determine the diffusion coefficient, the concentration and the molar fraction of oxidant of electrochemical active species simultaneously. Simultaneous determination method of concentration and diffusion coefficient is in particular extremely important in assay of the species in environmental sample. For example, after electrolysis of a certain substance by the twin electrode, we can determine diffusion coefficient and concentration of the products simultaneously. The determination of the concentration of the products after electrolysis means that the assay of the reactant which we cannot measure directly, is possible. For example, iron sulfide is insoluble in water, and we cannot usually measure iron sulfide for electrochemistry. However, we will be able to determine the concentration of ferric ion by applying this method after electrolytic oxidation in the twin electrode. Because the condition of solution changes after electrolysis, the diffusion coefficient of the ferric ion by this method might change. Even if such a case, for each sample we can determine the diffusion coefficient of the ferric ion by this method. Therefore, we can determine the concentration of ferric ion produced from iron sulfide in the environmental samples, and will report the topic in the next paper.

CHAPTER 3

RAPID DETERMINATION OF SOLID CONTENT IN THE SUSPENSION BY MEASUREMENT OF ELECTRICAL CONDUCTIVITY

3.1 Introduction

There are many occasions when solid content in a suspension needs to be determined, ranging from process control of industry to pollutant analysis of environmental sludge samples. The conventional dry-weight method for determining solid content in a suspension is not entirely satisfactory. It often requires long time (ca. 6 hours) and high temperature (105~110 °C) [82] for drying. This is disadvantageous to the on-line industry control, especially to the in situ monitor of pollutant in the sediment of sea and lake.

We are studying a rapid method for the determination of content of a reductive pollutant, such as iron sulfide (FeS) [83-86] in the seabed sludge. Usually the determination of content of pollutant in the sludge consists of two parts: one is evaluation of pollutant weight percent (wt%) in the wet sludge; the other is evaluation of solid wt% in the wet sludge. We recently have developed a new technique to determine the FeS wt% in the seabed sludge by electrochemical method with twin electrode in several minutes. In this case, it becomes quite important whether the estimation of solid wt% can be achieved in short time for the determination of FeS content in the solid component of the seabed sludge. Moreover, if solid wt% in the sludge can be determined by electrochemical method with twin electrode, we can perform the two measurements for a sludge sample within the same twin electrode.

Electrical conductivity has been employed for a number of years for the studies of suspensions.[87-91] Although the kinds of suspended particles varied from minerals[92-94] to biological cell,[95, 96] most of the studies suggested that the ratio of conductivity of the suspension to the disperse medium is a function of the volume fraction of the

dispersoids.[97-102] However, the investigation has never been applied to the real environmental sludge sample. The sample of seabed sludge is quite different from those of suspensions studied before. The ingredients of the sludge are complicated. The particle size and shape of the solids in the sludge are also complicated. Therefore, it is uncertain to apply the electrical conductivity to the study of seabed sludge.

The goal of the present work is to investigate the application of conductivity measurement to the determination of solid content in the suspension, especially in the real environmental sludge samples. We will report the rapid determination of solid content in the suspension by measurement of electrical conductivity. This will make it possible to attempt in situ measurement of FeS content in the seabed sludge by electrochemical method.

3.2 Experimental Section

3.2.1 Materials

All the reagents for dispersoids (see Table 3.1) were purchased from NACALAI TESQUE, INC. and were used without further purification. The reagents of NaCl and poly-vinylpyrrolidone (PVP) for disperse medium were also obtained from NACALAI TESQUE. Purified water prepared by Milli-Q (Millipore Corp.) was used for electrolyte solution.

3.2.2 Apparatus

IKA universal grinder M20 was purchased from IKA WORKS, INC. to crush the dispersoids. To make a uniform suspension, VORTEX-GENIE 2 (Scientific Industries, Inc.) was used. An ultrasonic bath 3210J-DTH (Branson Ultrasonics Corporation) was used to remove the bubbles in the suspension. We measured electrical conductivity by an MC126 conductivity meter (Mettler-Toledo) at 25.0 °C. The conductivity meter has been calibrated with standard solution of known conductivity before each conductivity measurement. The conventional drying process for determination of solid content in the sludge was performed in FM38 Muffle Furnace (Yamato Scientific Co. Ltd) at

105~110°C for 6 hours. A JFOL JSM-6400F scanning electron microscope (SEM) was used for scanning electron micrographs.

3.2.3 Methods

Suspension Preparation. Ten kinds of solids of slight soluble or insoluble in water, including oxides, salts, an element and a polymer, were chosen as dispersoids; These are described in Table 3.1. The substances except for carbon have been crushed for 3 minutes before making suspensions. For carbon (charcoal activated, untreated powder), the dispersoids were classified into two types: (1) being crushed for 3 minutes and (2) without being crushed. The disperse medium was electrolyte solution of 0.5M NaCl, containing PVP. Herein, PVP was used to achieve a viscosity sufficient of the disperse medium in order to prevent sedimentation of the dispersoids during the process of measurement. The solid fractional volume in the suspension was converted from the solid wt%t based on the densities of dispersoids and disperse medium. Herein, the density of the disperse medium is $1.01 g/cm^3$ at 25.0 °C, and the densities of dispersoids are shown in Table 3.1.

Table 3.1 Dispersoids and Their Density

type	solids	density / $g\ cm^{-3}$
oxide	SiO_2	2.65
	TiO_2	4.17
	MnO_2	5.03
	SnO_2	6.95
salt	$CaCO_3$	2.72
	$BaSO_4$	4.50
	FeS	4.70
	AgCl	5.56
element	carbon	2.25
polymer	polystyrene	1.06

Ten separate suspension samples were prepared by dispersing the solid powder into the disperse medium. All the samples were then treated with VORTEX to make the solid powder distribute uniformly throughout the suspension.

Sludge Sampling. The environmental sludge samples were taken by an Ekman dredge of 5141A (Rigosha & Co., Ltd,) from the seabed of Uranouchi Bay in Kochi, Japan. The sampling locations were shown in Figure 3.1.

The samples were passed through a stainless steel sieve of 2.0 mm hole-size to remove lump of remains of organisms. All the samples were then deaerated with presaturated argon and kept in brown bottles.

Measurement of Solid wt% of Sludge by Dry-weight Method. The determination of solid wt% in the sludge by conventional method is performed as follows: Weighted amount of sludge samples were dried at definite temperature (105~110 °C) to constant weight. Then solid wt% of the sludge sample was evaluated based on the ratio of mass weight after drying to that before drying.

Figure 3.1 A map of Uranouchi Bay in Kochi of Japan showing the sampling locations.

3.3 Results and Discussion

3.3.1 Electrical Conductivity of Suspension Sample

In order to investigate the relation between the electrical conductivity and the solid content in a suspension, the electric conductivity of the suspension with electrolyte has been measured for various kinds of dispersoids.

For SiO_2 suspension, a plot of the conductivity ratio, κ/κ_0, *vs.* solid fractional volume, V_f, is shown in Figure 3.2A, where κ and κ_0 are the specific conductivity of the suspension and the disperse medium, respectively. As can be seen in Figure 3.2A, the conductivity ratios decrease from unity with the increasing of SiO_2 fractional volume in the suspension. Theoretically, the plot of κ/κ_0 *vs.* V_f is a curve rather than a straight line, but within the surveyed range, it is possible to regard the plot as linear. A regression analysis gives a best fit of slope = -1.72 with correlation coefficient $R^2 = 0.98$ to the linear relation between κ/κ_0 and V_f for SiO_2 suspension. According to the linear relation, the fractional volume of SiO_2 in the suspension can be determined from the conductivity ratio. Base on the value of V_f, we can readily evaluate SiO_2 wt% in the suspension with density of SiO_2 powder (see Table 3.1).

For dispersoids of FeS and polystyrene, experimental data also suggest good linear relations between the conductivity ratio and the solid fractional volume, which are shown in Figures 3.2B and 3.2C. Regression analyses give slopes of -1.83 and -1.69 with $R^2 = 0.96$ and 0.98 to the suspensions of FeS and polystyrene, respectively. For the suspensions of SiO_2, FeS and polystyrene, the slopes of their curves are similar. This indicates that it is possible to evaluate the fractional volume of mixture of SiO_2, FeS and polystyrene in the suspension by conductivity measurement, irrespective of the proportion of three components in the mixture.

A

y = -1.72 x + 1.00
$R^2 = 0.98$

κ/κ_0

V_f

B

y = -1.83 x + 1.00
$R^2 = 0.96$

κ/κ_0

V_f
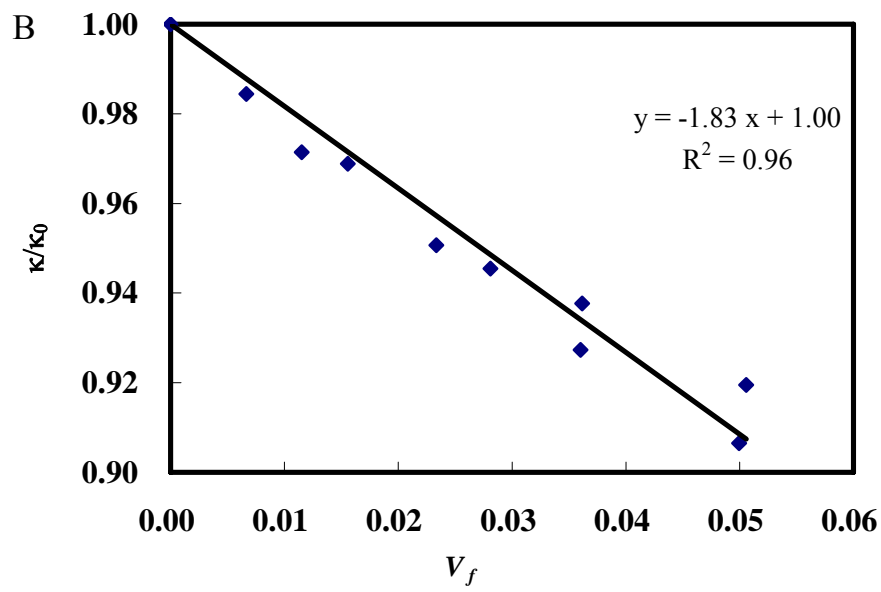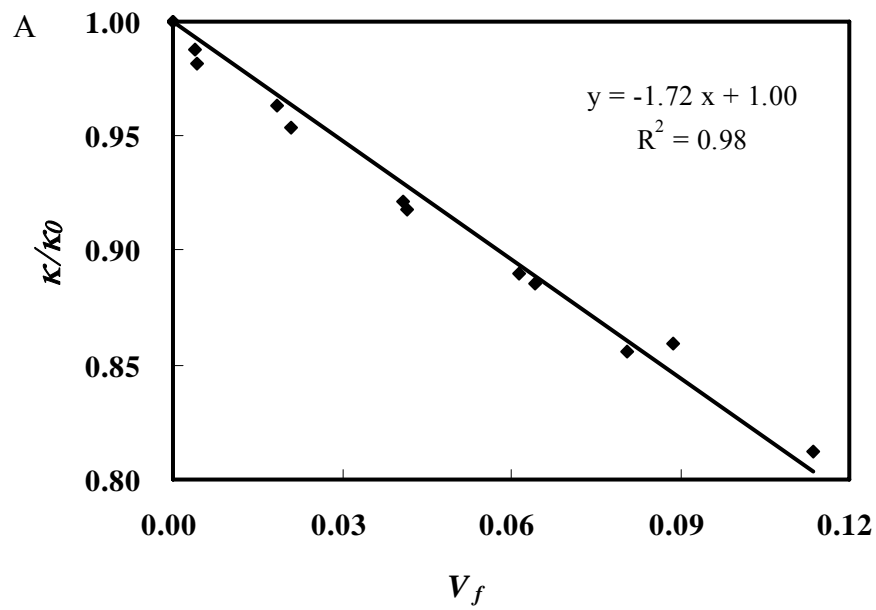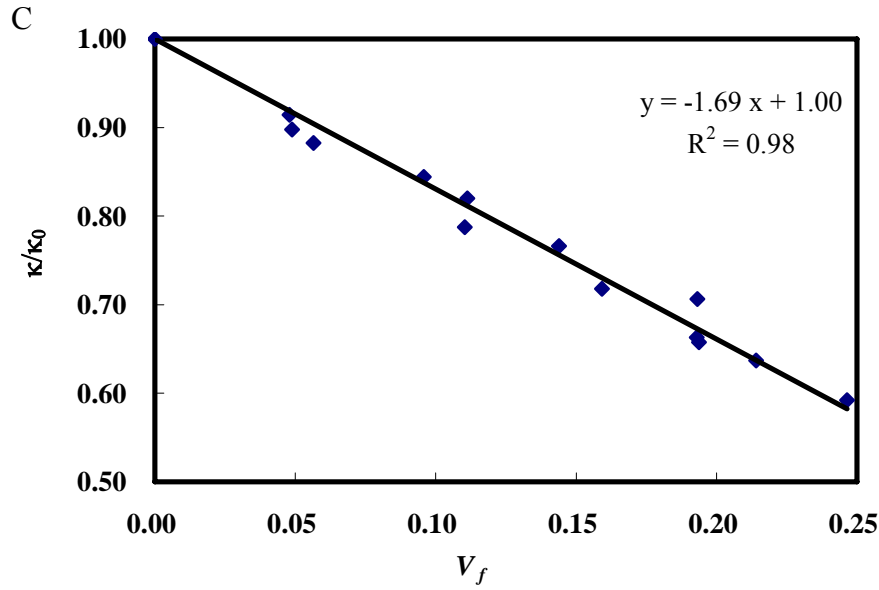
Figure 3.2 Conductivity ratio as a function of the fractional volume V_f for different dispersoids: (A) SiO_2; (B) FeS; (C) polystyrene.

When the conductivity ratio, κ/κ_0, is plotted against V_f for other seven kinds of dispersoids (see Table 3.1), same trends are observed. The slopes and correlation coefficient (R^2) of the linear relations for various suspensions, are listed in Table 3.2. The overall values of R^2 for the suspensions with different dispersoids are quite high (≥ 0.96), indicating that there is a linear relation between the conductivity ratio and the solid fractional volume within a certain range of V_f for all the suspensions. The slopes of the plots vary from -2.66 for carbon suspension to -1.32 for AgCl system. The dispersoids of carbon, SnO_2 and AgCl show somewhat deviations of slopes, compared with other solids (see bold characters in Table 3.2). It does not yet appear possible to give a clear interpretation to these deviations, since many factors may contribute to the reasons, such as the geometrical factors of the particles, the internal conductance of the dispersoids and the solubility change of suspended solid in a NaCl solution.[103]

Table 3.2 Regression Coefficients (Slope and Correlation Coefficient) of the Relations of κ/κ_0 vs. V_f for Various Dispersoids

dispersoids	slope	R^2
SiO_2	-1.72	0.98
TiO_2	-2.10	0.99
MnO_2	-1.66	0.97
SnO_2	**-2.34**	0.99
$CaCO_3$	-1.99	0.97
$BaSO_4$	-2.02	0.97
FeS	-1.83	0.96
AgCl	**-1.32**	0.99
carbon [a]	**-2.66**	0.97
Polystyrene	-1.69	0.98

[a] Carbon has been crushed for 3 minutes.

When we compare all the experimental data of suspensions surveyed together in Figure 3.3, we observe an approximate linear relation between κ/κ_0 and V_f. A linear regression analysis of these data, leads to a line of best fit of slope = -1.79 with R^2= 0.97. According to this linear relation, we can propose an empirical equation for any kinds of dispersoids by

$$\kappa/\kappa_0 = 1 + aV_f \qquad (0 \leq V_f < ca.0.25) \qquad (3.1)$$

where the parameter a stands for a slope and takes the value of -1.79 corresponding to the linear regression analysis, and V_f is the fractional volume of any kinds of solids in the suspension.

On the basis of eq 3.1, we can estimate the solid fractional volume V_f in a suspension through conductivity measurement. Then according to the fractional volume and the density of the solid, the solid wt% in the suspension can be readily evaluated.
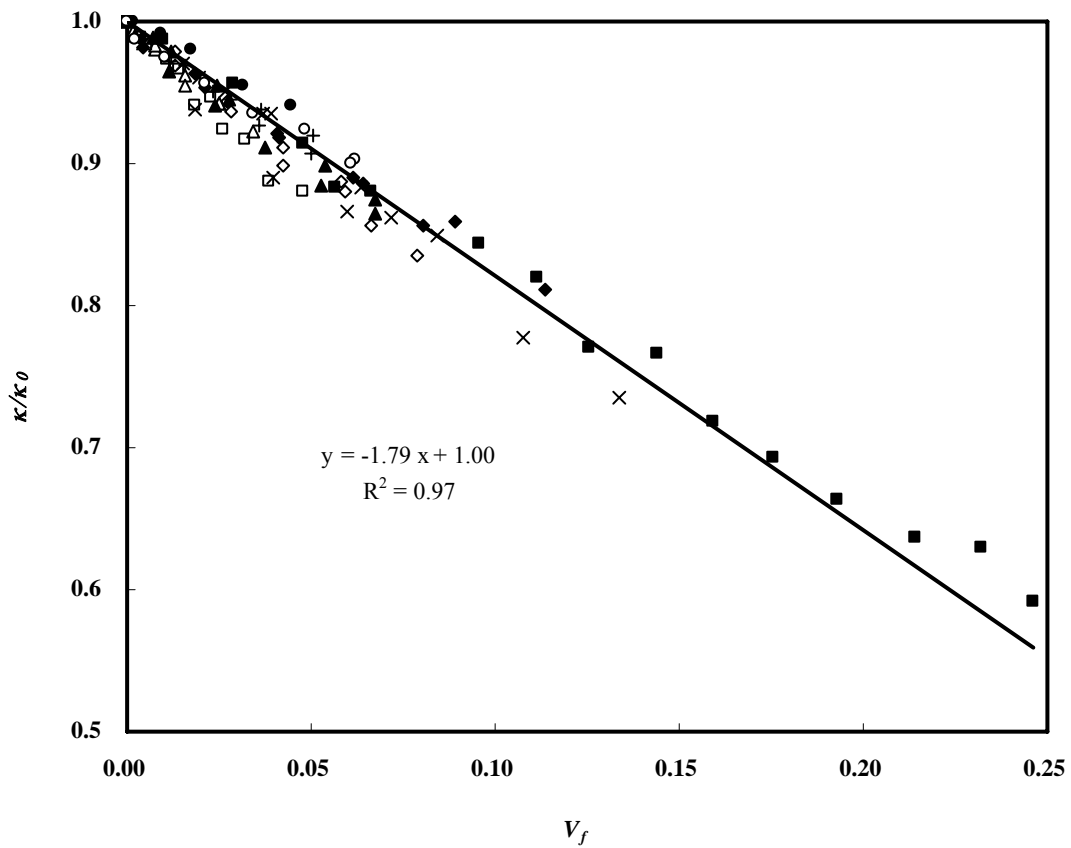
Figure 3.3 Conductivity ratio as a function of the solid fractional volume for ten kinds of dispersoids: (◇) TiO_2; (◆) SiO_2; (△) SnO_2; (▲) $BaSO_4$; (×) $CaCO_3$; (●) AgCl; (+) FeS; (□) cabon; (■) polystyrene; (○) MnO_2.

3.3.2 Determination of Solid Content in Sludge Sample

To validate the conductivity method, we apply it to the determination of solid wt% in the samples of seabed sludge, which are collected from Uranouchi Bay. The sampling

points are shown in Figure 3.1. We determine the solid wt% in these samples by both conventional dry-weight method and the proposed conductivity method. Herein, for conductivity method, we employ eq 1 with $a = -1.79$ to evaluate the solid fractional volume in the sludge sample by conductivity measurement,[104] and then convert it to the solid wt% with a density of 2.20 g /cm^3 for the dry sludge.

Figure 3.4A shows the results of solid wt% measured by conductivity method, in comparison with those by conventional dry-weight method. We observe a good agreement between the two methods, excluding samples 10 and 11. There are large amount of sands in samples 10 and 11, so that it is difficult to form uniformly suspentions. For this reason, the conductivity method gives an underestimation of samples 10 and 11 compared with those by conventional dry-weight method.

B

$$y = 1.03 x - 0.19$$
$$R^2 = 0.93$$

Solid wt% by dry -weight method

Solid wt% by conductivity method
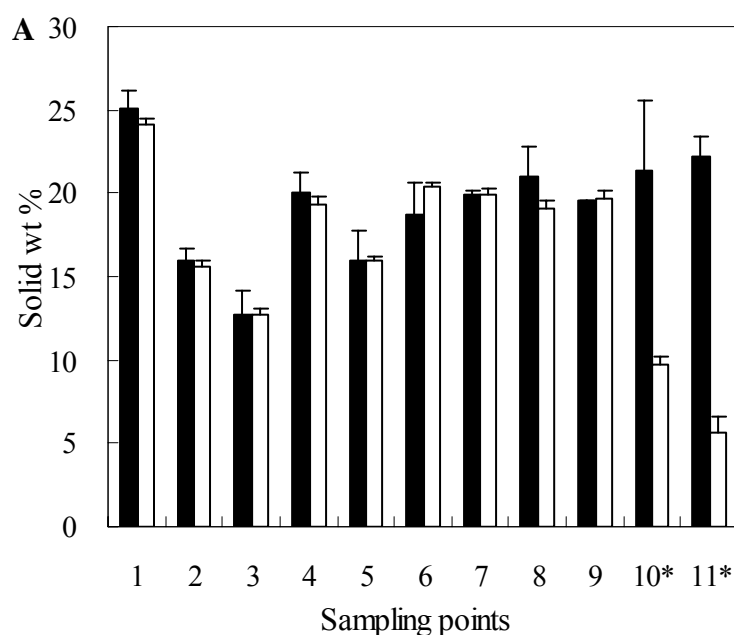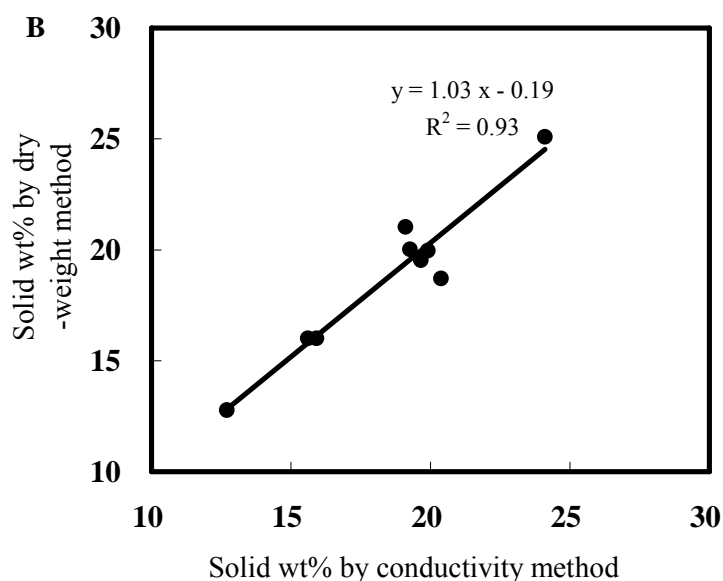
Figure 3.4 Measurement results of solid wt% in the seabed sludge by the conductivity method and the conventional dry-weight method. (A) Comparison between both methods for samples 1-11. Black column: conventional dry-weight method; White column: conductivity method. The samples 10* and 11* contain a large amount of sands. (B) Correlation of both methods for the samples excluding 10* and 11*.

For samples 1-9, however, a highly significant correlation ($R^2=0.93$) between the two methods is obtained (see Figure 3.4B). The almost unity slope value of 1.03 indicates that both methods are accurately measuring the same value of solid wt%. A paired *t*-test [105] is employed to further ascertain whether the observed difference between the two methods for samples 1-9 is significant. When the significance level is set of 0.05 with a two-sided *t-test*, a critical t-value of $t_{0.025,8} = 2.31$ is obtained. In this study, t-value is less than the critical t-value ($|t| = 0.845 < 2.31$), indicating there is no significant difference between both methods for the determination of solid wt% in the general sludge.

These results prove that it is reliable to determining the solid wt% in the seabed sludge by conductivity measurement. More importantly, if the conductivity measurement can be performed by twin electrode, we can combine this technique with the usual analysis of electroactive species by twin electrode. In this case, it will be

possible to determine the content of pollutant in the solid component of the seabed sludge with twin electrode.

3.3.3 A Comparison of Empirical Equation with Maxwell-Wagner Equation

To obtain a better understanding of the conductivity method, we have compared the empirical equation with Maxwell-Wagner equation, which is widely used as a theoretical conductivity model for heterogeneous systems and expressed by [106]

$$\kappa = \kappa_0 \frac{\kappa_s + f\kappa_0 - fV_f(\kappa_0 - \kappa_s)}{\kappa_s + f\kappa_0 + V_f(\kappa_0 - \kappa_s)} \tag{3.2}.$$

Herein, κ_s is the electrical conductivity of the dry dispersoid and f is a factor which is relevant to the shape of dispersoid in a suspension. The other symbols have their same meaning as previous. When internal conductance of the dispersoids is neglected by assuming $\kappa_s = 0$, eq 3.2 becomes

$$\frac{\kappa}{\kappa_0} = \frac{1 - V_f}{1 + \dfrac{V_f}{f}} \tag{3.3}.$$

According to the study of H. Fricke, [106, 107] f gets a maximum value of 2 for spherical particle. With the particle shape changing from spherical to rod-like, the value of f decreases.

A comparison of eq 3.1 with eq 3.3 is shown in Figure 3.5 for the relation of conductivity ratio against the solid fractional volume. As can be seen, the curve from empirical equation (curve *d*) shows similar trend to that from Maxwell-Wagner equation on condition of $f = 2$ (curve *a*), but the deviation between their slopes is not small. This deviation may be due to the value of f. The Maxwell-Wagner equation with $f = 2$ (curve *a*) represents a case of spherical dispersoids, whereas the actual particle shapes in the suspensions are various, rather than solely spherical. The empirical equation (curve *d*)

reflects an average case of the various shapes of particles, so that there is deviation between curves *a* and *d*. Fricke's experiments [106] provide a support for this prediction through estimating factor *f* of sand suspensions. In that case, factor *f* got average value of 1.392 for the Maxwell-Wagner equation, corresponding to curve *b* in Figure 3.5. The deviation between curves *b* and *d* is smaller than that between curves *a* and *d*, demonstrating that the curve slope of the Maxwell-Wagner equation is dependent on the value of *f*.
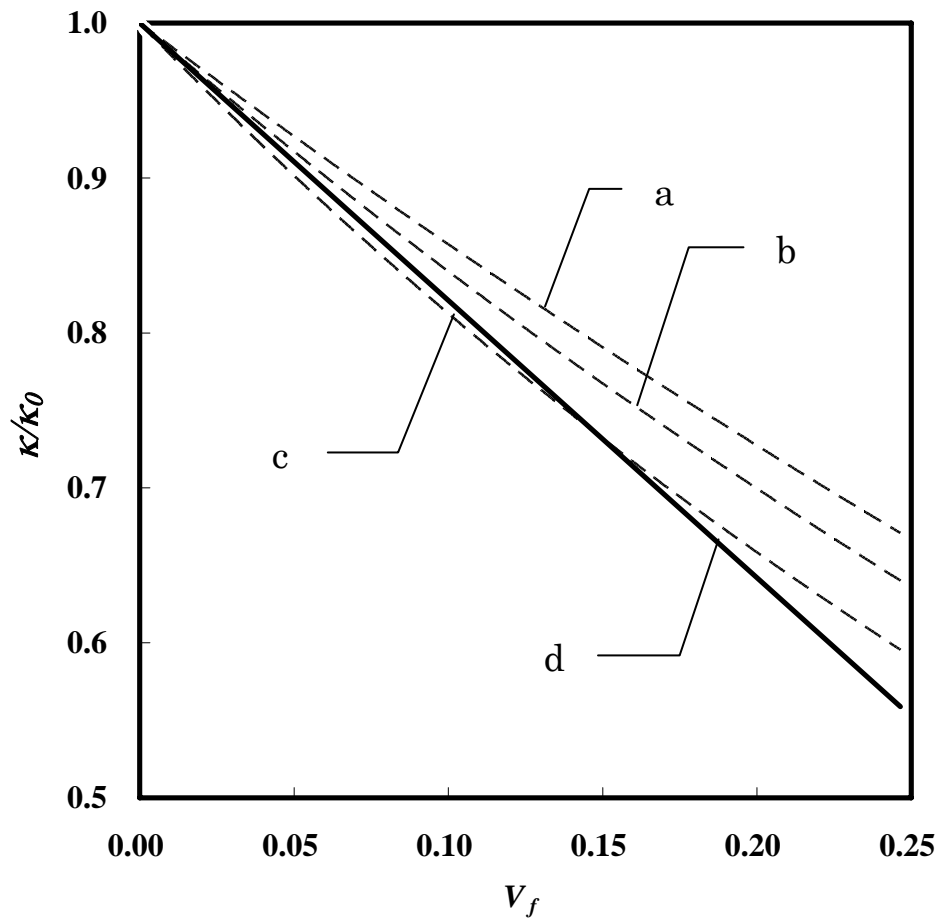

Figure 3.5 Comparison of empirical equation with Maxwell-Wagner equation. The full and dotted lines represent the calculated values according to eqs 3.1 and 3.3: (a) eq 3.3 with *f* = 2; (b) eq 3.3 with *f* = 1.392; (c) eq 3.3 with *f* = 0.929; (d) eq 3.1.

When making a curve fitting of the Maxwell-Wagner equation to the overall data in Figure 3.3, we obtain f value of 0.929. In this case, the Maxwell-Wagner equation with f = 0.929 (curve c) shows a very good agreement with the empirical equation (curve d) in Figure 3.5. It indicates that the empirical equation is substantially consistent with the Maxwell-Wagner equation for predicting the relation between the conductivity ratio and the solid fractional volume in the suspension within the surveyed range. Indeed, with eq 3.3 of f = 0.929 to evaluate the solid content in the sludge, we can obtain an almost same result as that with the empirical equation (refer to Figure 3.4). This suggests that it is possible to estimate the solid content in the seabed sludge by conductivity measurement with either of the equations.

3.3.4 Behaviors of Conductive Dispersoids in the Suspension

When measuring suspensions with conductive dispersoids, the conductivity ratio increases from unity with increasing solid fractional volume, unlike the situations shown in Figure 3.2. In Figure 3.6, curve a shows such increasing trend for carbon suspension. Some researchers have reported the similar electrical property of suspensions with conductive dispersoids. [94, 102] In the present study, however, we find that even for conductive dispersoids such as carbon, when the particles have been crushed, the suspension shows the similar trend to those of insulating dispersoids for the plot of conductivity ratio $vs.$ solid fractional volume (See data sets of carbon in Figure 3.3 and curve b in Figure 3.6). For other conductive dispersoids, such as SnO_2 and MnO_2, their suspensions show the similar situations to that of carbon (See data sets in Figure 3.3).
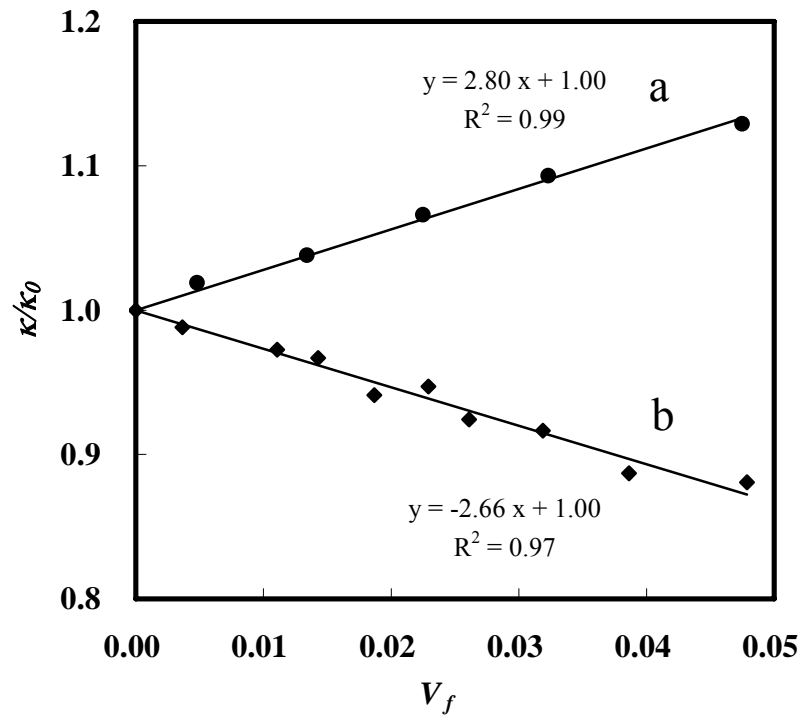
Figure 3.6 Conductivity ratio for carbon suspension as a function of the fractional volume V_f with different treatments of dispersoids: (a) without crush; (b) with crush.

To get a further understanding for this phenomenon, SEM (scanning electron microscopy) images of carbon dispersoids are shown in Figure 3.7. The light gray parts in the SEM pictures correspond to the carbon particles. When carbon dispersoids are not crushed, certain amounts of particles show relatively large and rod-like (see Image I); Some particle sizes are more than 100μm. After being dispersed into the medium, these carbon particles may act as a short-circuit path for current flow (short-circuit effect), [108] so that the conductivity ratio increases (curve *a* in Figure 3.6). However, when carbon dispersoids have been crushed, the ratio of rod-like particles to the whole powders remarkably decreases and most particles show spherical (see Image II); Many particle size approaches to 50 μm. This may be disadvantageous to the short-circuit effect, so that carbon particles behavior like the insulating dispersoids. As a result, conductivity ratios inversely decrease (curve *b* in Figure 3.6). For conductive dispersoids, particle size and shape may play an important role in the conductivity property of suspension.

Although the behaviors of the conductive dispersoids need more systematic studies, the unclear mechanism does not invalidate the application of the proposed conductivity method to the determination of solid wt% in the seabed sludge, because the main component of the seabed sludge is SiO_2 which has no conductance. Even though some other conductive particles may exist in the seabed sludge, since the particle size of the seabed silt is quite small ($\frac{1}{16} \sim \frac{1}{256}$ mm) [5] which approaches to or less than the particle size after treatment of crush in this study, we do not need to consider the situation of curve a in the Figure 3.6 when applying the empirical equation to the determination of solid wt% in the seabed sludge.

Image I

| $\times 50$ | $\times 350$ |

Image II

| $\times 50$ | $\times 350$ |
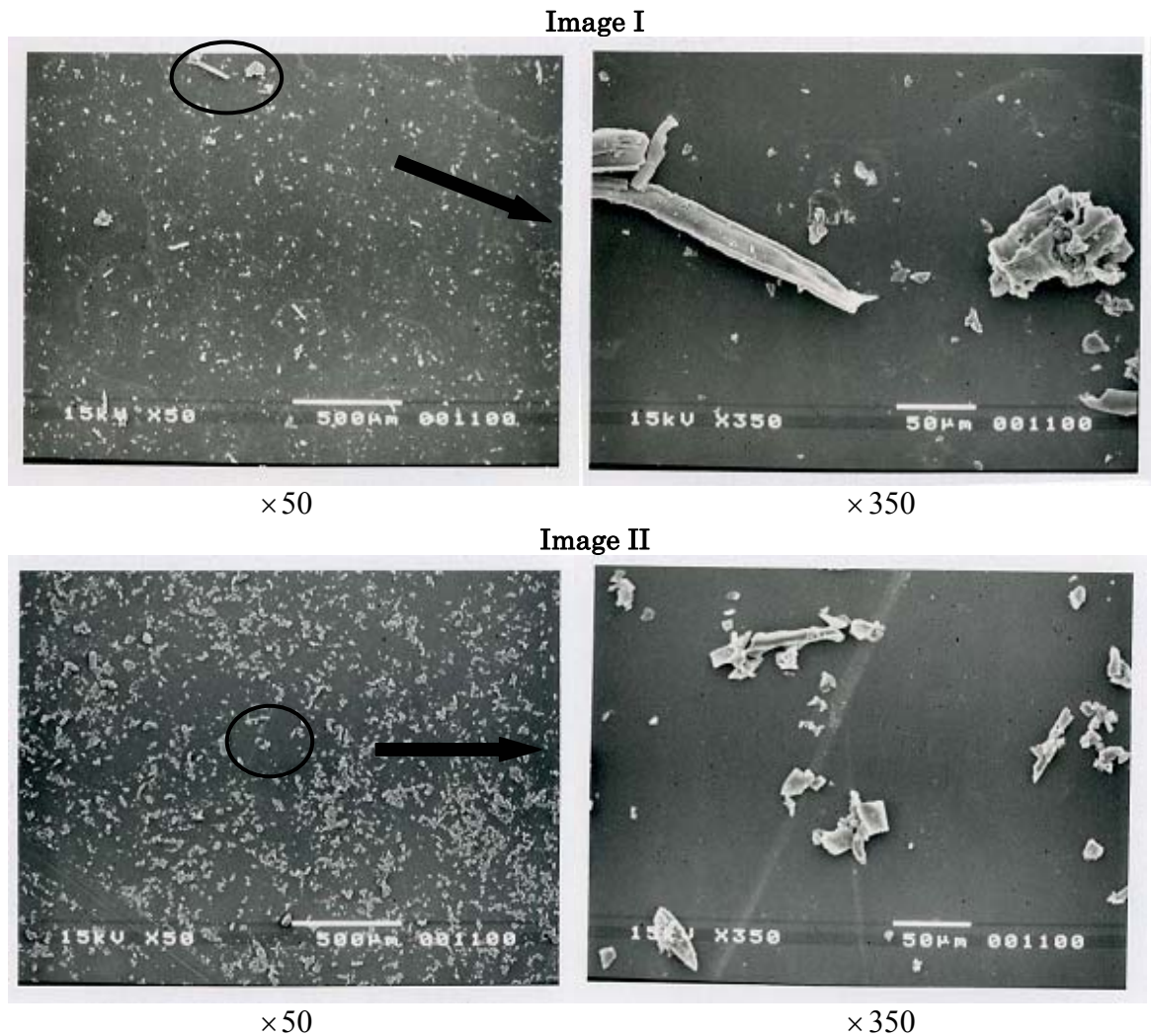
Figure 3.7 SEM images of carbon dispersoids with treatment of crush (Image I) and no crush (Image II). The right images show the magnification of the circled parts in the left

images.

3.4 Conclusions

The dependency of conductivity ratio on the solid fractional volume was investigated in various suspensions. We found a linear relation between the conductivity ratio and the dispersoid fractional volume within the range of V_f ($0 \leq V_f <$ ca. 0.25). According to this fact, an empirical equation was proposed. On the basis of the equation, the solid wt% in the suspension can be easily determined by conductivity measurement.

The conductivity method proposed in this study has been applied to the real seabed sludge. The measurements of solid wt% by conductivity method agreed well with those by conventional dry-weight method. Therefore, we can evaluate the solid wt% in the sludge with the conductivity method. More importantly, if the specific conductivity can be measured by twin electrode, the conductivity method can be applied to the various occasions. As is known, many electroactive species can be measured with twin electrode cell. In that case, it is possible to combine the measurements of solid wt% and species amount in the suspension within the same twin electrode. This is quite useful to the in situ measurement of pollutant content in the solid component of the seabed sludge by electrochemical method, such as the determination of iron sulfide content which will be reported in other paper.

CHAPTER 4

A NEW ELECTROCHEMICAL TECHNIQUE BY TWIN ELECTRODE FOR ASSAY OF IRON SULFIDE IN SEABED SLUDGE OF BAY

4.1 Introduction

In the location where water flow is poor, such as in a bay, at the early stage aerobic bacterium is active due to eutrophication caused by inflow of domestic and industrial wastewater, resulting in an anoxic condition. For anoxic water-body, the bottom sludge becomes anaerobic owing to the action of aerobe, following that anaerobic bacteria become active. The anaerobic bacteria metabolize the organic compound and sulfate, resulting in the generation of sulfide ion. By incorporating with ferrous ion in the seawater, the sulfide ion forms iron sulfide, which gradually precipitates to the bottom and accumulates in the sediment. When iron sulfide slightly dissolves in the water, it will react with dissolved oxygen, accelerating the consumption of oxygen. Apparently, such reduction of oxygen is different from that by aerobic bacterium.

When fresh nutrient comes into the water-body, anaerobic bacterium produces sulfide again, which follows the accumulation of iron sulfide in seabed sludge. By this way, a vicious circle takes place. The anoxic condition of the water which forms due to the vicious circle gives remarkable damage to the growth of underwater plant and benthos such as shellfish and lobster, and finally makes harmful influence upon the whole ecosystem in the bay. Thus, it is important to measure the content of iron sulfide in the seabed sludge from the viewpoint of water quality survey as well as an investigation of reduced condition in the seabed sludge.

However, it is usually accompanied with troublesome process to assay drying solid weight and sulfide amount to evaluate the quantity of iron sulfide in the seabed sludge. There are many problems such as long measurement time, large energy consumption (high temperature and long time for drying and distillation), use of reagent with large

environmental load (strong acid and reducing agent) as well as high cost for assay.

In this chapter, we report a new technique that can determines the iron sulfide content in the solid component of seabed sludge by electrochemical method with a twin electrode. This technique has three features described as follows:

1. With a twin electrode, solid wt% in seabed sludge can be evaluated by conductivity measurement.

2. With the same twin electrode, we perform electrolytic oxidation of the sludge at 2V (*vs*. SCE) for a given time, converting slightly soluble iron sulfide into soluble ferric ion.

3. With the same twin electrode, the concentration of ferric ion is determined by chronoamperometry. According to this, iron sulfide wt% in the sludge can be evaluated.

Finally based on the ratio of iron sulfide wt% (from step 3) to the solid wt% (from step 1), we can determine the iron sulfide content in the solid component of seabed sludge. We will also discuss the validity of the proposed technique.

4.2 Experimental Section

4.2.1 Materials and Sample Preparation

All the reagents, except for iron disulfide (FeS_2), were purchased from Nacalai Tesque, Inc. and used without further purification. Reagent FeS_2 was purchased from Kishida Chem. Inc.. Solutions were prepared using deionized water by Milli-Q system (Millipore Corp.).

Artificial sludge samples were made by uniformly dispersing FeS-SiO_2mixture powder into a disperse medium. The reagents of FeS and SiO_2 have been crushed for 3 minutes before use; the disperse medium was made by dissolving poly-vinylpyrrolidone (PVP) into NaCl solution. Herein, PVP was used to achieve a viscosity sufficient of the disperse medium to prevent sedimentation of the dispersoids during the process of measurement, as illustrated in Chapter 3.

4.2.2 Apparatus

A platinum disk electrode served as indicator electrode for cyclic voltammetry; for

other electrochemical experiments, such as electrolysis and chronoamperometry, a twin electrode was used as working electrodes, which was composed of two platinum plates purchased from Nilaco Co., with an effective area of $4 cm^2$ and a clearance of $300 \mu m$. For the construction of twin electrode in detail, it has been described in Chapter 2. A saturated calomel electrode (SCE) and a platinum wire ring were used in this study as the reference and auxiliary electrodes, respectively. Dual Potentiostat, BAS Co., was employed in chronoamperometry. The current of working electrode was recorded with a digital recorder (Yokogawa, DL708). An electrochemical analyzer of BAS100B/W (CV-50W) was used in cyclic voltammetry.

We performed electrical conductivity measurement with a Kohlrausch circuit, of which twin elecrode was used as electrolytic cell and the alternating current was obtained from Model 458A function generator (Kikusui Electronic Corp.). A Model LT364L oscillator was provided by Iwatsu Electric Co. Ltd..

4.2.3 Electrochemical Method

The electrolysis experiment was performed with twin electrode at 2V for one minute. In carrying out the chronoamperometry for determination of ferric ion concentration, the potential of electrode 1 was stepped from 0.7V to 0.3 V with keeping the electrode 2 at 0.7V (*vs.* SCE). Before each experiment, the samples were deoxygenated with bubbling argon. The working electrode has been polished with $0.05 \mu m$ alumina powder (BAS Co.) on a wet pad wetted with Milli-Q water. All measurements were made at 25°C.

4.2.4 Chemical Analytical Method

Chemical analytical method for determination of iron sulfide ($FeS+FeS_2$) in the wet sludge sample of lake was carried out by utilizing the chemical method for analysis of acid volatile sulfide (AVS) and chromium-reducible sulfur (CRS).[55-60] After addition of acid and reducing agents to the sediment sample, the produced H_2S was sparged with argon to a trapping solution, which was followed by the determination of sulfide in the trapping solution through iodimetric analysis. The amount of solid content in the wet

sample was determined separately with dry-weight method.

4.2.5 Sludge Sampling

The real environmental seabed sludge samples were taken by an Ekman dredge of 5141A (Rigosha & Co. Ltd.) from Uranouchi Bay in Kochi, Japan. The sampling locations, same as that in Chapter 3, were shown in Figure 4.1.

Figure 4.1 A map of Uranouchi Bay in Kochi of Japan showing the sampling locations.

The samples were passed through a stainless steel sieve of 2.0 mm hole-size to remove lump of remains of organisms, then deaerated with presaturated argon and kept in brown bottles.

## 4.3 Results and Discussion

4.3.1 Generation of Iron (III) Ion from the Electrolytic Oxidation of Iron Sulfide in the Seabed Sludge

The bottom sludge of a bay, due to the influence of human being, contains reductive pollutant such as iron (II) sulfide, and shows anaerobic condition. It will be useful to investigate the extent of reductive pollution if the reductive pollutant can be analyzed

electrochemically. We collected the wet seabed sludge containing seawater, and placed a platinum electrode into the suspension sample to perform a cyclic voltammetry. The experimental results are shown in Figure 4.2A. The concentration of electrochemical active species in the sludge suspension is so low that by normal cyclic voltammetry, electrochemical response can not be observed (see Figure 4.2 Aa). However, we observed a large reversible response for the cyclic voltammetry after applying the potential of 2V (*vs*. SCE) to the working electrode for one minute. The peak consists with that in the cyclic voltammogram of ferrous ion (see Figure 4.2 Ab), suggesting that the ferric ion may originate from the iron (II) sulfide in the seabed sludge after electrolytic oxidation. To confirm this prediction, the following experiments were carried out.

We dispersed the crushed iron sulfide into a 0.5M NaCl aqueous solution and performed a similar cyclic voltammetry (see Figure 4.2 B) as in the seabed sludge sample. Before electrolytic oxidation, the electroactive species can not be observed, as shown in Figure 4.2 Ba, while after electrolytic oxidation at 2V for one minute, we observe the potential response from ferric ion (see Figure 4.2Bb) same as that in the seabed sludge. We carried out similar experiment for ferriferous oxide and iron oxide, but the peak of ferric ion was not observed even if the electrolytic oxidation was employed. This is due to the fact that further oxidation can not occur at 2V for the insoluble ferric compound, so that ferric ion does not elute.
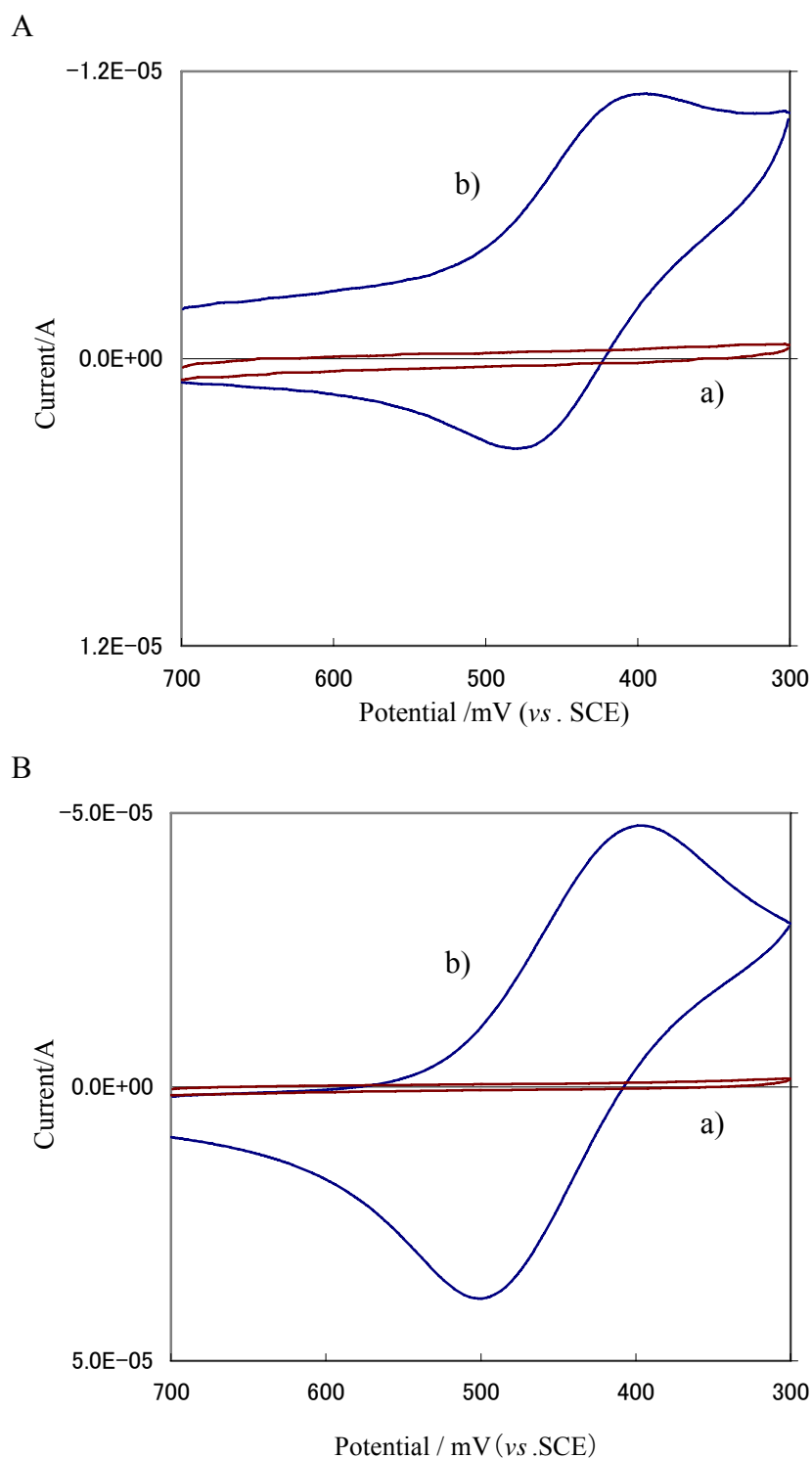
Figure 4.2 Cyclic voltammogram of different samples at 25°C with scan rate = 100 mV/s. (A) Seabed sludge: a) before electrolytic oxidation, and b) after electrolytic oxidation at 2V for one minute. (B) Iron sulfide suspension: a) before electrolytic oxidation, and b) after electrolytic oxidation at 2V for one minute.

4.3.2 *Determination of Concentration of Ferric Ion by Chronoamperometry with Twin Electrode*

We performed electrolytic oxidation with twin electrode, so that the dissolved ferric ion was confined to an interval space between the two working electrodes of twin electrode without diffusion to outside. In this case, the concentration of ferric ion does not vary with time during the process of measurement, and we can measure the concentration of ferric ion by chronoamperometry with the twin electrode. The following shows an example of measurement.

We disperse the crushed iron sulfide in a 0.5M NaCl aqueous solution containing polyvinylpyrrolidone to prepare the suspension of 0.3wt% iron sulfide. The twin electrode is placed into the suspension at 25˚C, and is applied the potential of 2.0 V (*vs.* SCE) for one minute. After electrolytic oxidation, the ferric ion dissolves and its concentration is measured by chronoamperometry with the twin electrode. A sigmoid current-time curve in chronoamperometry is obtained as shown in Figure 4.3A. Based on the contact of tangent line that is drawn from origin for the sigmoid curve, we can determine suspension diffusion coefficient and the ferric ion concentration simultaneously. For this technique, it has been reported in Chapter 2. The slopes of the lines that are drawn from origin for every point of the sigmoid current-time curve in Figure 4.3A, is expressed as [current/ time], i/t. The [current/ time]-time curve has an extreme value as shown as a peak of the curve in Figure 4.3B. As mentioned in Chapter 2, we have the following two equations for the extreme value i_{ex}/ t_{ex} at time t_{ex} :

Time in extreme value:

$$\frac{Dt_{ex}}{L^2} = 0.166675 \tag{4.1}$$

The extreme value:

$$\frac{\dfrac{i_{ex}L^2}{nFADC}}{t_{ex}} = 3.70035 \tag{4.2}$$

where D is the diffusion coefficient of electrochemically active species, L is the distance between the two working electrodes in the twin electrode, n is the number of electrons transferred in the redox reaction, A is the electrode area, and C is the concentration of electroactive species. In Figure 4.3, the extreme value of [current/ time] is 3.39 μA/sec in t_{ex}= 33.6 sec. The diffusion coefficient of ferric ion is then determined from eq 4.1 (D= 4.44×10^{-6} cm^2/ sec), and ferric ion concentration is obtained from eq 4.2 (C= 4.88mM). By this way, therefore, we can determine the concentration of the ferric ion which is generated from the electrolytic oxidation of iron sulfide by twin electrode.
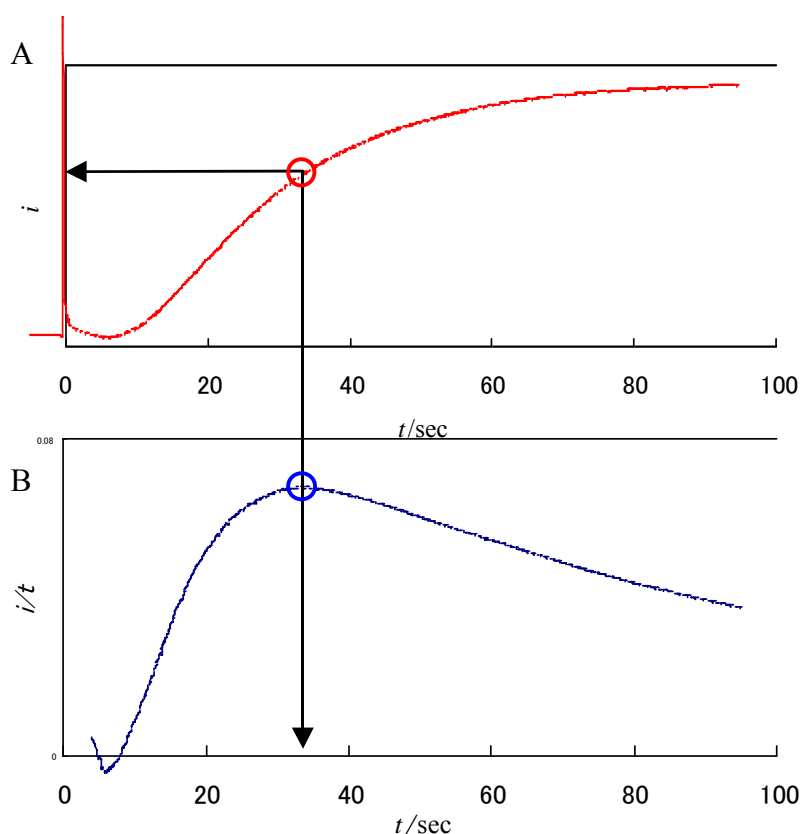
Figure 4.3 Determination of concentration of ferric ion in the suspension containing 0.3wt% iron sulfide by chronoamperometry after the electrolytic oxidation of sample at 2V for one minute. (A) current-time curve; (B) [current/ time]-time curve.
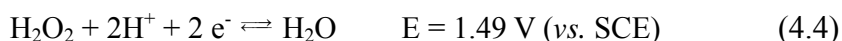
4.3.3 Mechanism for Generation of Ferric Ion from the Electrolytic Oxidation of Iron Sulfide in Suspension

Dependency of generation of ferric ion on the oxidation potential. Since iron(II)

sulfide is slightly soluble in water, it is difficult to electrolyze it on the electrode surface directly. However, iron sulfide can be easily oxidized by the hydrogen peroxide which is generated from the oxidization of water on the platinum electrode. This processes can be described as eqs 4.3 and 4.4.

$$3 \; H_2O_2 + 2 \; FeS + 6 \; H_2O \rightarrow 2 \; Fe^{3+} + 2 \; S^0 + 6 \; OH^- \tag{4.3}$$
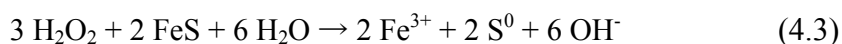
Redox potential is 1.49V (*vs.* SCE) for the generation of hydrogen peroxide from oxidation of water:

$$H_2O_2 + 2H^+ + 2 \; e^- \rightleftharpoons H_2O \qquad E = 1.49 \; V \; (\textit{vs. SCE}) \tag{4.4}$$

At pH= 7, the redox potential in eq 4.4 becomes 1.08V. When we apply the electrolytic oxidation to a suspension sample containing 0.3wt% iron (II) sulfide with twin electrode for one minute, the dependency of generation of ferric ion on the oxidation potential is shown in Figure 4.4. We found that the concentration of ferric ion increases with the oxidation potential from the vicinity of 1V to the vicinity of 2V (vs. SCE). This is due to the fact that at the potential of the vicinity of 1V, hydrogen peroxide begins to form on the electrode, so that iron sulfide is oxidized and ferric ion dissolves into the suspension. With the increasing of oxidation potential, hydrogen peroxide increases, so that ferric ion concentration increases. Stable measured value for ferric ion concentration is not provided at potential higher than 2V, owing to the generation of oxygen on the twin electrode surface. Therefore, the potential is set at 2.0V (vs. SCE) to perform the electrolytic oxidation of iron (II) sulfide.
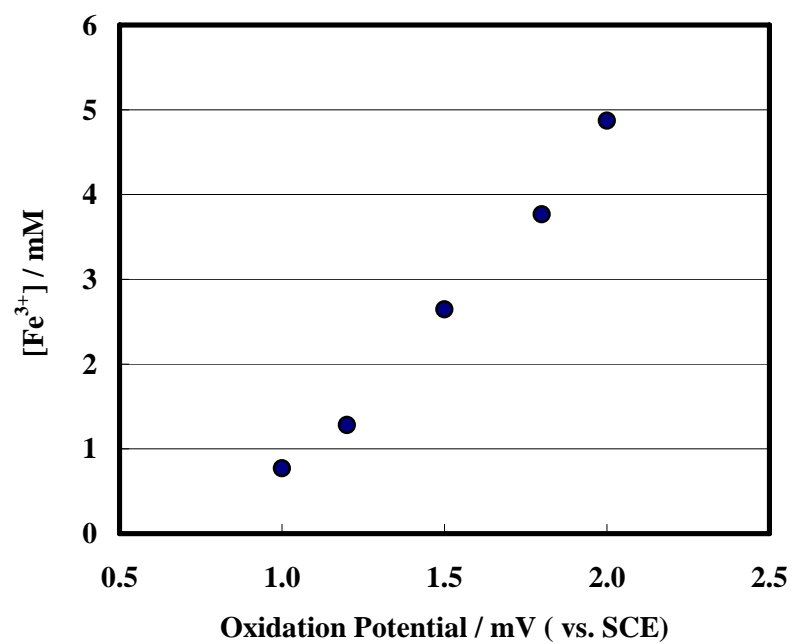
Figure 4.4 Dependency of generation of ferric ion on the oxidation potential.
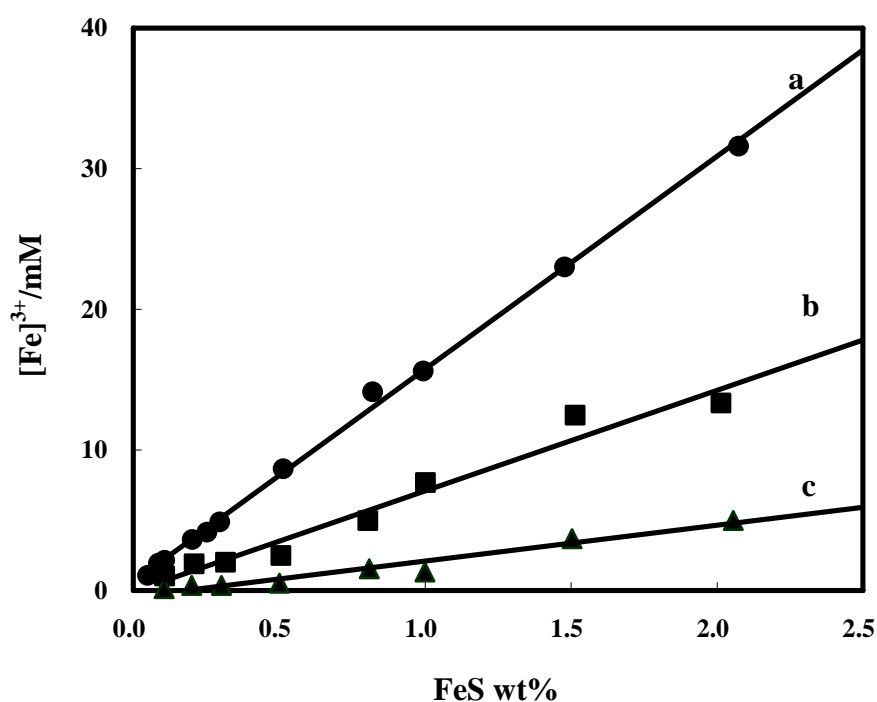
Dependency of generation of ferric ion on the oxidation time. The amount of hydrogen peroxide produced by the electrolytic oxidation at potential of 2V (*vs.* SCE) is in proportion to electrolytic oxidation time. Since the amount of ferric ion produced is proportional to the amount of hydrogen peroxide, the measured concentration of ferric ion is in proportion to the electrolytic oxidation time. A plot of the concentration of produced ferric ion *vs.* electrolytic oxidation time exhibits a good linear relationship as shown in Figure 4.5. The slope of this straight line associates with the parameter of electrode area *A*, distance between the twin electrode *L*, as well as the potential of the electrolytic oxidation. For a given condition where the three parameters have been preset, the amount of hydrogen peroxide produced should be constant. In this case, the oxidation rate is only dependent on the amount of iron (II) sulfide in the suspension during a given time of electrolytic oxidation.
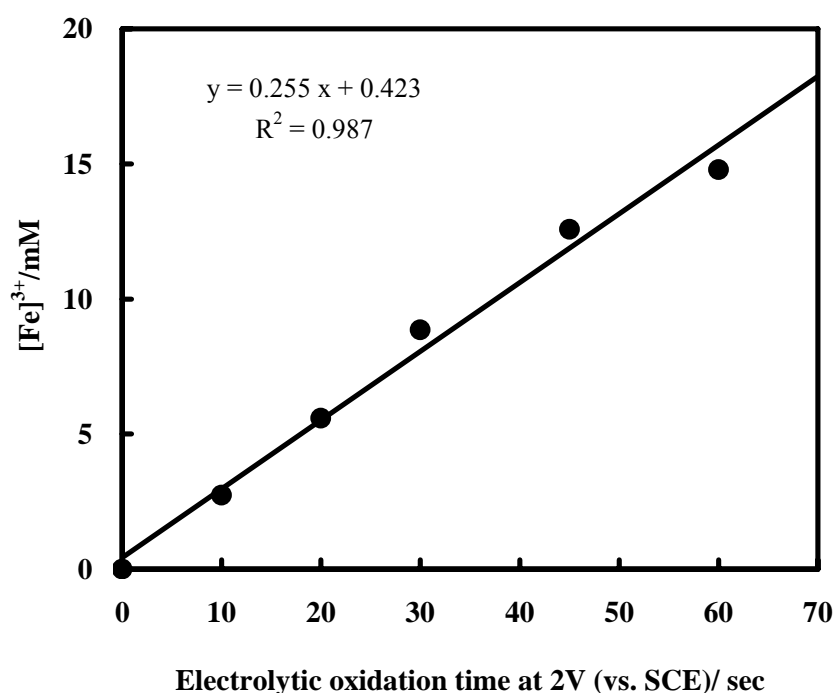
Figure 4.5 Dependency of generation of ferric ion on oxidation time with oxidation potential at 2V (*vs.* SCE).

Dependency of generation of ferric ion on iron (II) sulfide wt% in the suspension. We examined the dependency of the concentration of the ferric ion on iron (II) sulfide wt% in the suspension at the following conditions: (1) the distance between the twin

electrode L= 300µm; (2) the electrode area A = 4cm^2; (3) the electrolytic oxidation potential of 2V (*vs.* SCE); and (4) the electrolytic oxidation time for 10sec, 30sec, and 60sec. With increasing of iron sulfide wt %, the ferric ion concentration increases linearly, as shown in Figure 4.6. For same iron sulfide wt%, longer the electrolytic oxidation time, larger is the amounts of hydrogen peroxide, so that the slope of the linear relation becomes larger (see curves *a, b* and *c* in Figure 4.6). Current value in the electrolysis experiment is so large that the concentration of produced hydrogen peroxide is extremely high. The actual amount of ferric ion is lower enough than those should be produced by hydrogen peroxide and iron sulfide according to the reaction of eq 4.3, indicating that the generated hydrogen peroxide can not oxidize all of the iron(II) sulfide in the suspension within the given electrolytic oxidation time. That is, not all of iron sulfide in the suspension is oxidazed. Thus, the amount of ferric ion depends on the rate of reaction between hydrogen peroxide and iron sulfide. Figure 4.6 shows that the reaction rate is in proportion to the concentration of hydrogen peroxide and the amount of iron(II) sulfide in the suspension. For an unknown suspension sample, we can estimate the iron (II) sulfide amount from the measured ferric ion concentration after electrolytic oxidation at 2V for one minute when we regard the curve *a* in Figure 4.6 as a calibration one.


Figure 4.6 Dependency of generation of ferric ion on the iron(II) sulfide wt% in the

suspension with different oxidation time: (a) 60 seconds; (b) 30 seconds; and (c) 10 seconds.

4.3.4 Correlation between the Concentration of Ferric Ion and Iron Sulfide wt% in the FeS-SiO$_2$ Suspension System

In the real seabed sludge, except for iron (II) sulfide, there are often other solid materials. It is necessary to confirm whether the calibration curve in Figure 4.6a is applicable to the suspension sample, when the electrochemically inactive solid except iron sulfide is contained in the sample. Herein, we use silicon dioxide (SiO$_2$) as an electrochemically inactive solid together with iron (II) sulfide to prepare for artificial seabed sludge sample. Then the correlation between the ferric ion concentration and the iron (II) sulfide wt% in the artificial seabed sludge samples is shown in Figure 4.7 when the amount of iron (II) sulfide content in total solid component correspond to 10% and 1%, respectively. The horizontal scales represent the iron(II) sulfide wt% and solid wt% in the suspension. In Figure 4.7, dotted lines show a straight line of Figure 4.6a. For a suspension containing other solid except for iron(II) sulfide, we observe a good linear relationship between the ferric ion concentration and FeS wt% when the amount of iron(II) sulfide is not so large. Although the content of iron(II) sulfide in the total solid component varies, the slope of the relationships are almost same as that in Figure 4.6a. For the region where the amount of iron(II) sulfide in the suspension is large, deviation from the straight line is observed. Also, the yellow substance was identified on the electrode after experiment. This may be attributed to the deposition of sulfur on the surface of electrode. In this case, the surface of electrode becomes partially inactive, and the concentration of ferric ion can not be measured reproductively. Therefore, it is desirable that the measured concentration of ferric ion should be less than 2mM when the linear relation in Figure 4.6a is employed as a calibration curve to the unknown samples.
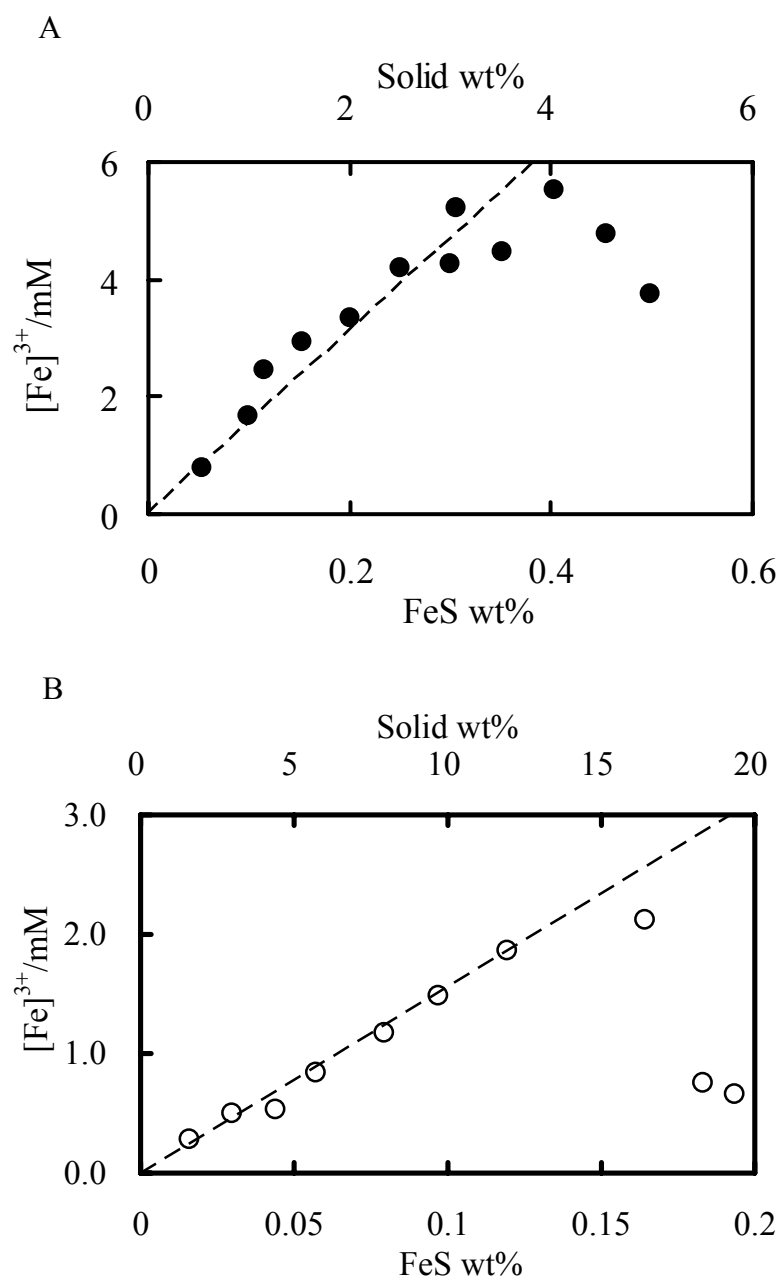
Figure 4.7 Correlation between the concentration of ferric ion and the FeS wt% in the artificial seabed sludge of FeS-SiO$_2$ suspension system with different weight percent of FeS content in the total solid component (FeS and SiO$_2$): (A) 10%; and (B) 1%.

### *4.3.5 Determination of Solid wt% by Conductometry with Twin Electrode*

It is impossible to determine the content of iron(II) sulfide in the solid component if the solid wt% can not be evaluated, even though the evaluation of iron(II) sulfide wt% in the suspension can be performed. Thus, we have to determine the solid wt% in the suspension with the twin electrode. In Chapter 3 we have already described *the first calibration curve* $\kappa/\kappa_0 = 1 + aV_f \ (0 \leq V_f < ca.0.25)$, by which the solid wt% can be determined based on the electric conductivity ratio of suspension to disperse medium. Generally, the electric conductivity is measured by conductivity meter, but we can evaluate the conductivity ratio with the twin electrode. Herein, *Kohlrausch circuit* is constructed to determine the conductivity ratio. Figure 4.8 shows a relationship between conductivity ratio and solid % by volume. When this relationship is compared with that obtained by conductivity meter, the almost same results are obtained. That means the volume % of solid in the suspension can be determined by measuring the ratio of electric conductivity of suspension and disperse medium with the twin electrode. Then the solid wt% can be evaluated from the solid volume % by considering the solid density, as shown in eq 4.5.

$$W_f = \frac{V_f D_s}{[(1-V_f)D_m + V_f D_s]} \tag{4.5}$$

where W_f and V_f are weight fraction and volume fraction in a suspension, respectively; D_s and D_m are densities of dry dispersoids and disperse medium, respectively.

The above discussions mean that we can determine the solid wt% of a suspension which is inside the twin electrode before the suspension sample is electrolytically oxidized with the same twin electrode. Then, according to the ratio between FeS wt% evaluated based on the concentration of ferric ion after electrolytic oxidation, and the solid wt% evaluated by electric conductivity measurement before the electrolytic oxidation, we can finally determine the iron(II) sulfide content in the solid component with only twin electrode.
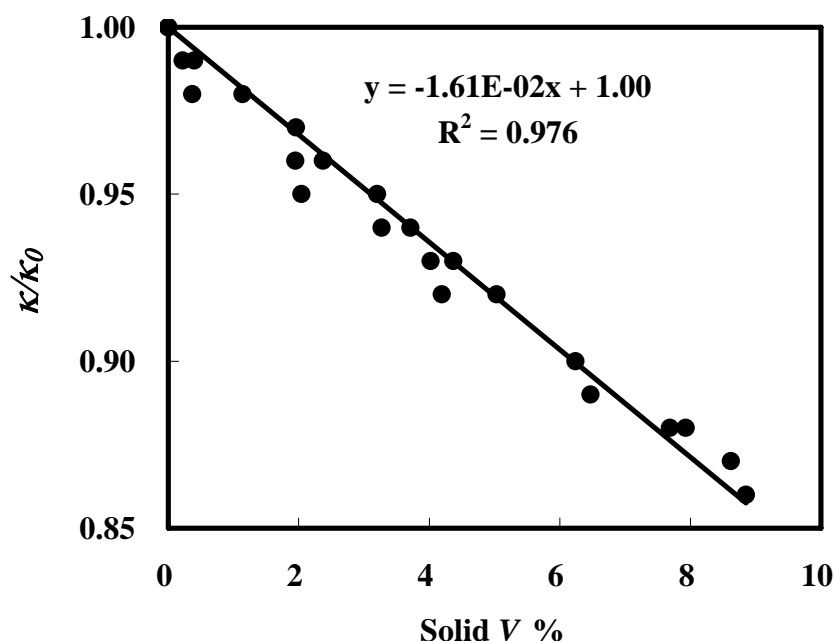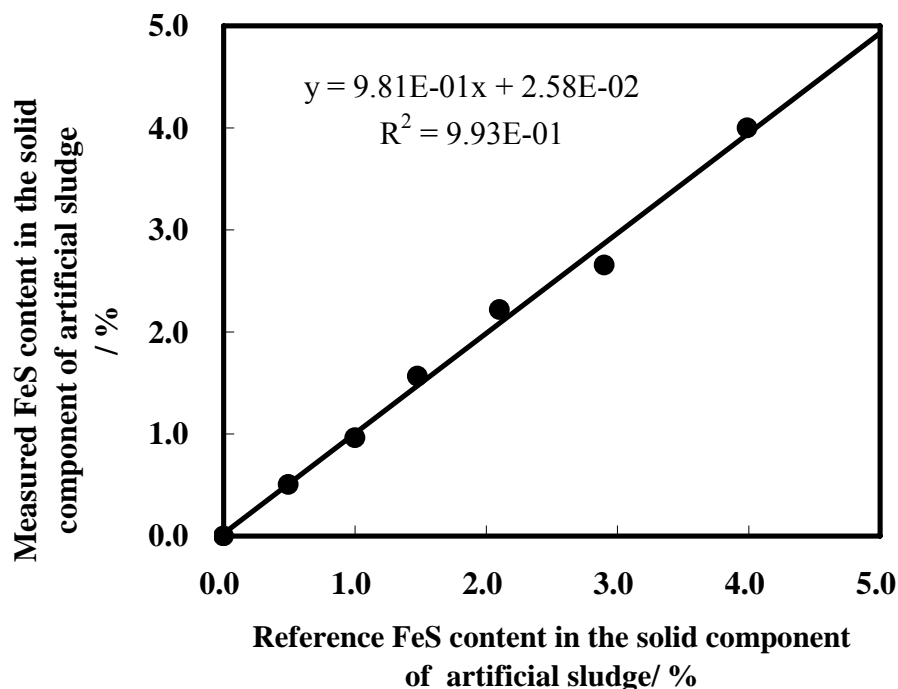
Figure 4.8 Correlation between the conductivity ratio and the solid volume percent in a suspension, with twin electrode for conductivity measurement.

4.3.6 Determination of Iron(II) Sulfide Content in the Artificial Seabed Sludge

We regard FeS/SiO_2 suspension system as artificial seabed sludge, of which 10% of total solid content with various FeS content are made in the suspension. We determine the FeS content in the solid component of the artificial seabed sludge by the proposed method. In this case, the plot in Figure 4.8 is employed as the calibration curve for determination of solid volume%; and the curve *a* in Figure 4.6 is used as the calibration curve for the determination of FeS wt% in a suspension.

We compare the measured FeS content by electrochemical method with the known value by preparation for the artificial sludge in Figure 4.9. A good linear relation was obtained, which passed though the origin with a slope of 0.981 and correlation coefficient $R^2=0.993$. It indicates that the proposed method is effective for the sample of artificial seabed sludge. Additionally, it means that the two calibration curves from Figure 4.8 and Figure 4.6a are reliable in the serial processes of determination of iron(II) sulfide content

in the artificial sludge.

Figure 4.9 Correlation between the measured result by electrochemical method and the reference value by preparation of sample for the determination of iron sulfide content in the solid component of the artificial seabed sludge.

4.3.7 Determination of Iron(II) Sulfide Content in the Seabed Sludge of Uranouchi Bay

To validate the proposed method further, the determination of iron sulfide content in the real seabed sludge was carried out. The samples were collected from the Uranouchi Bay in Kochi of Japan, and were measured by two methods of the chemical method and the proposed electrochemical method, respectively. The correlations between them were shown in Figure 4.10. We found that both methods gave measured values of almost same order of magnitude for the determination of iron(II) sulfide content, over the range of 0.3~ 2.0 mg/g by chemical method and 0.7~ 7.0mg/g by electrochemical method.

However, for all the samples except sample 8, electrochemical method gave higher evaluations than the chemical method did for the same sample. Also, the correlation

between them is low. For example, it was shown that by electrochemical method, samples 1-2 contained large amount of iron sulfide content compared with samples 7-9, but by chemical method, the iron sulfide content in samples1-2 were not so different from those in samples 7-9.
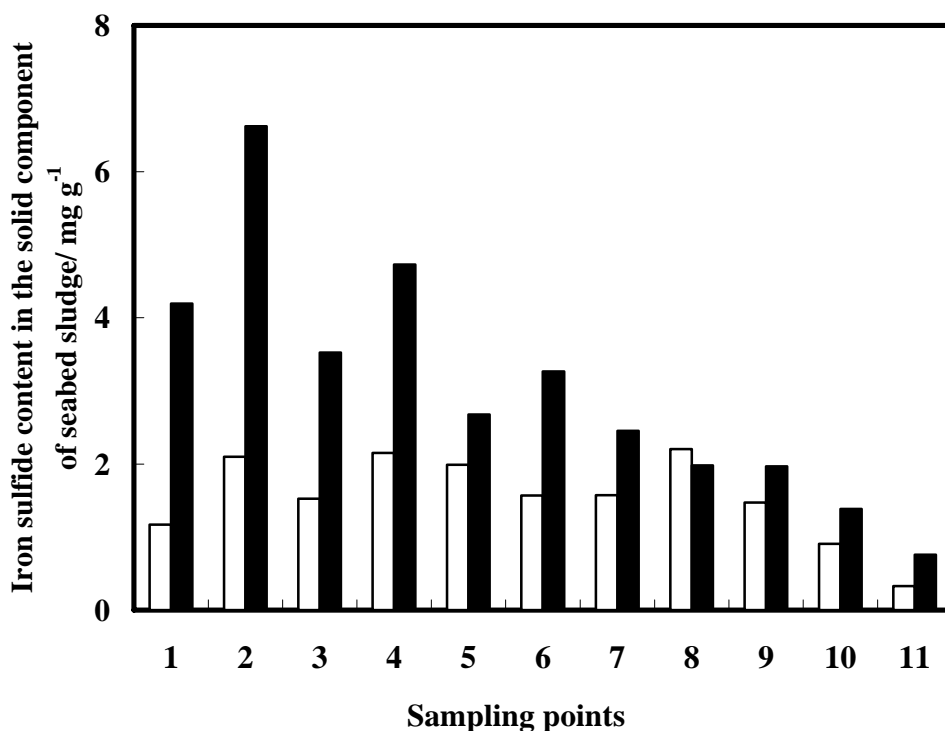
Figure 4.10 Comparison between the electrochemical method and the chemical method for the determination of iron sulfide content in the solid component of seabed sludge from Uranouchi Bay. Black column: content of iron sulfide (FeS+FeS$_2$) measured by electrochemical method; White column: content of iron sulfide (only FeS) measured by chemical method.

In fact, in addition of iron(II) sulfide, there is iron disulfide in the seabed sludge. In electrochemical analysis, the iron disulfide is oxidized by the hydrogen peroxide which is produced by electrolysis, thus leading to the generation of ferric ion. However, in chemical analysis, without reducing the iron disulfide beforehand, we cannot determine the amount of sulfide which comes from the iron disulfide. When the concentration of ferric ion from both iron(II) sulfide and iron disulfide was measured in an electrochemical analysis, in contrast, we evaluated the sulfide only from iron(II) sulfide by a chemical

analysis, so that the deviation occurred between the electrochemical method and the chemical method for the determination of iron sulfide content in the real seabed sludge , as shown in Figure 4.10. Therefore, it is necessary to investigate the influence of iron disulfide when employing the proposed electrochemical method to the real seabed sludge samples.

4.3.8 Generation of Ferric Ion from the Electrolytic Oxidation of Iron Disulfide in the Suspension

To confirm whether iron disulfide will influence the generation of ferric ion under the condition of electrolysis same as that for iron(II) sulfide, we carried out the experiments as shown in Figure 4.11. By comparing the dependency of concentration of ferric ion on the oxidation potential and time, we found similar behaviors when using 0.3wt% iron(II) sulfide suspension and 0.3wt% iron disulfide suspension as studied samples, respectively. This means that under the same electrolysis condition, such as same potential and oxidation time, both iron(II) sulfide and iron disulfide contribute to the generation of ferric ion. This prediction was confirmed by the experimental result shown in Figure 4.12. We found that dispersoids of iron(II) sulfide and iron disulfide indeed have the similar influence on the generation of ferric ion when oxidation of suspension was performed at 2V for one minute. Figures 4.12A and 4.12B show the linear relation between the concentration of ferric ion and the weight percent for iron(II) sulfide and iron disulfide, respectively. The slope values are 11.2 and 11.5, which are almost same for two different suspension samples, indicating that iron(II) sulfide and iron disulfide give the same contribution to the generation of ferric ion. Thus, it is reasonable to determine the weight percent of FeS and FeS_2 in the suspension using either calibration curve in Figures 4.12. It can be assumed that the measured iron sulfide content by electrochemical method as shown in Figure 4.10 corresponds to the total amount of iron sulfide (FeS and FeS_2) in the sludge.

A
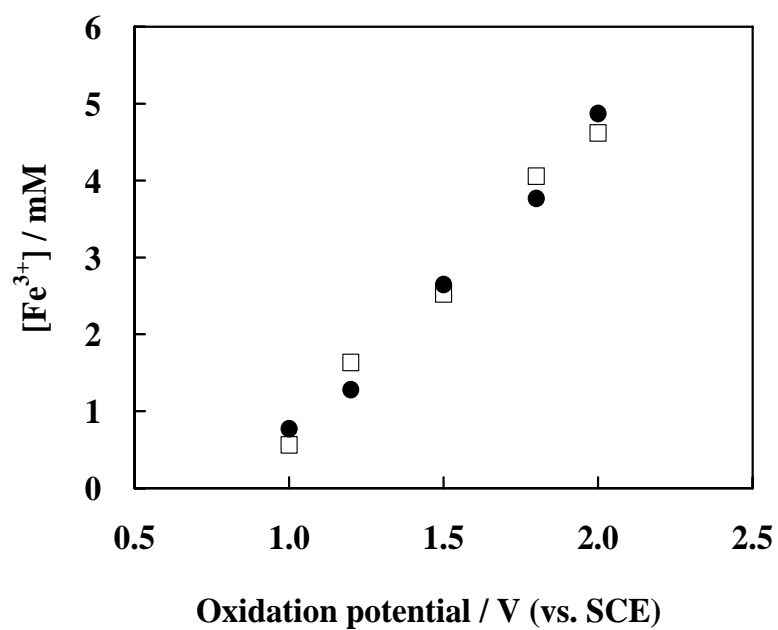
B
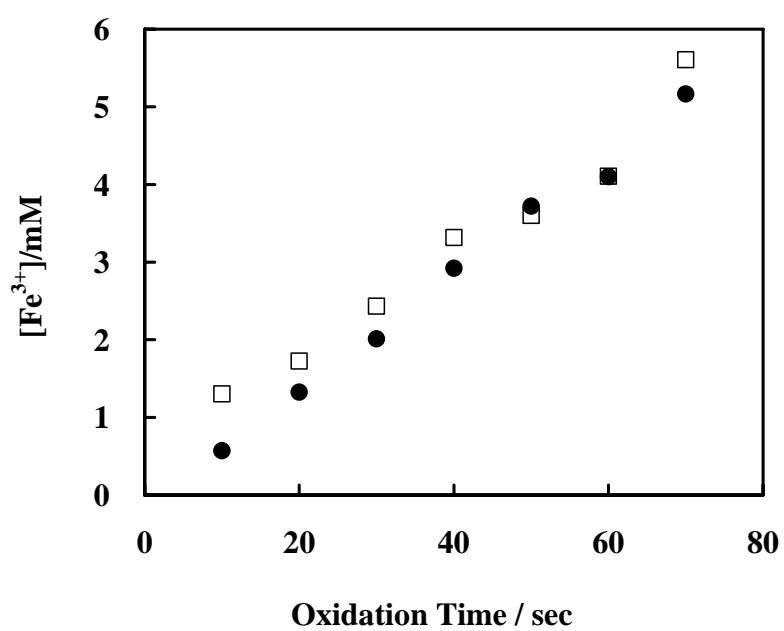
Figure 4.11 Dependency of concentration of ferric ion on oxidation condition of (A) electrolytic potential when oxidation time being one minute; (B) electrolytic oxidation time when potential being at 2V for 0.3 wt% suspension of (●) FeS and (□) FeS_2, respectively.

A

$$y = 1.12E+01x + 4.70E-01$$
$$R^2 = 9.92E-01$$

[Fe^{3+}] /mM

FeS wt%

B

$$y = 1.15E+01x + 2.07E+00$$
$$R^2 = 9.76E-01$$

[Fe^{3+}]/mM

FeS$_2$wt%
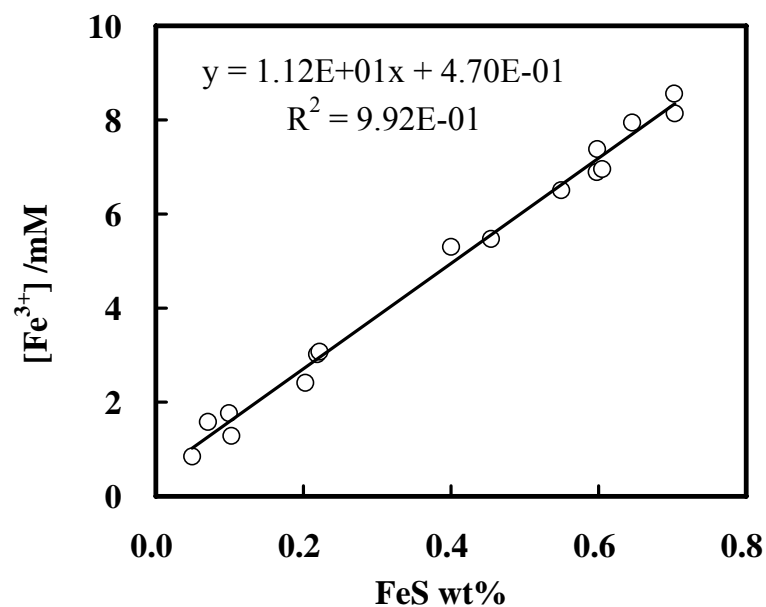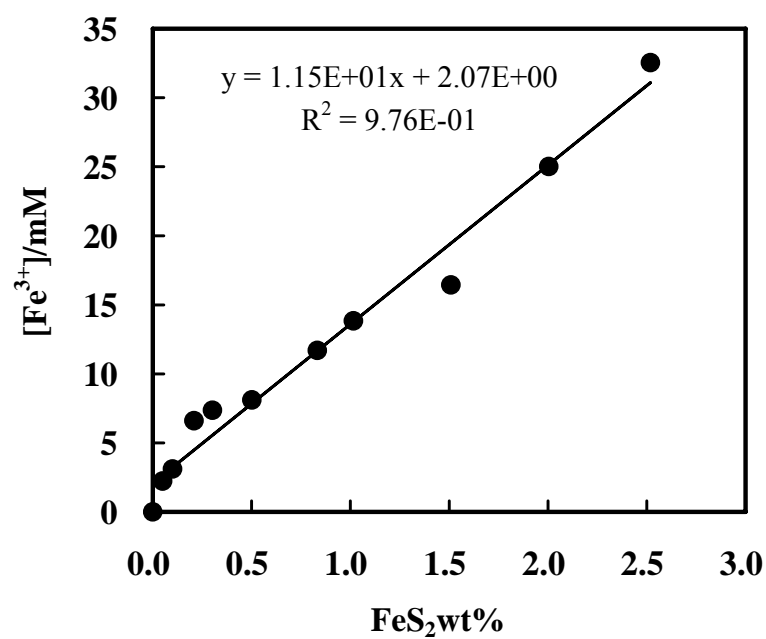
Figure 4.12 Relationship between the concentration of ferric ion and the weight percent of (A) FeS, and (B) FeS$_2$ in the suspension, respectively.

4.3.9 Determination of total content of Iron(II) Sulfide and Iron Disulfide in the Seabed Sludge

In the bottom of a bay where reducing conditions predominate, the black color of the sludge comes from iron (II) sulfide and iron disulfide. Pyritization in anoxic conditions often occurs by reaction between H_2S or $S(0)$ (as S_8 or polysulfides [S_x^{2-}]) and aqueous (or solid) FeS according to eqs 4.6 and 4.7.

$$FeS_{aq} + H_2S_{aq} \rightarrow FeS_2 + H_{2g} \tag{4.6}$$

$$FeS_{aq} + S_x^{2-}[orS_8] \rightarrow FeS_2 + S_{(x-1)}^{2-}[or7/8S_8] \tag{4.7}$$

We sampled the seabed sludge again from the same points as shown in Figure 4.1, and analyzed the content of iron(II) sulfide and iron disulfide by chemical analytical method. The experimental result was shown in Figure 4.13A. It was found that the profile of iron(II) sulfide content shown in Figure 4.13A resembles well that shown in Figure 4.10. Additionally, in Figure 4.13A, the difference in iron(II) sulfide content between samples 1-2 and samples 7-9 is not so large, while the difference in iron disulfide content between the samples 1-2 and the samples 7-9 is remarkably large. This may explain the observation in Figure 4.10, that is, the measured iron sulfide content by electrochemical method co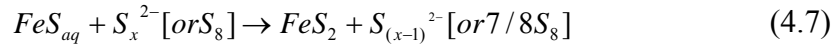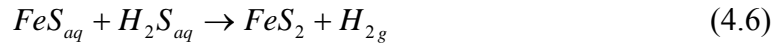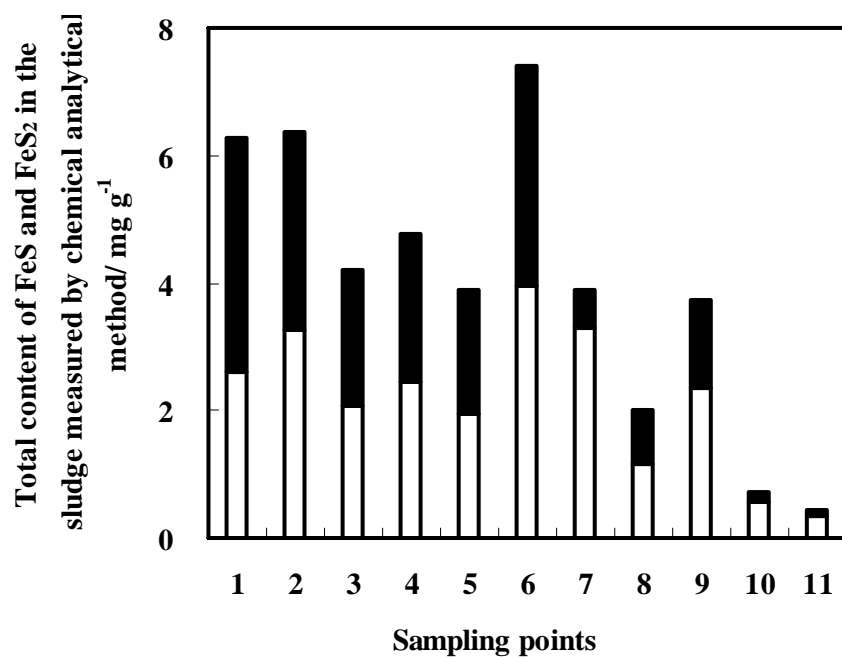rresponds to the total amount of iron(II) sulfide and iron disulfide, so that in Figure 4.10, the measured result by electrochemical method is larger than that by chemical method. The correlation of measurement between by two methods becomes better when considering the existence of iron disulfide, as shown in the inserted picture in Figure 4.13B.

A

B

$y = 1.61E+00x - 1.02E+00$
$R^2 = 9.32E-01$
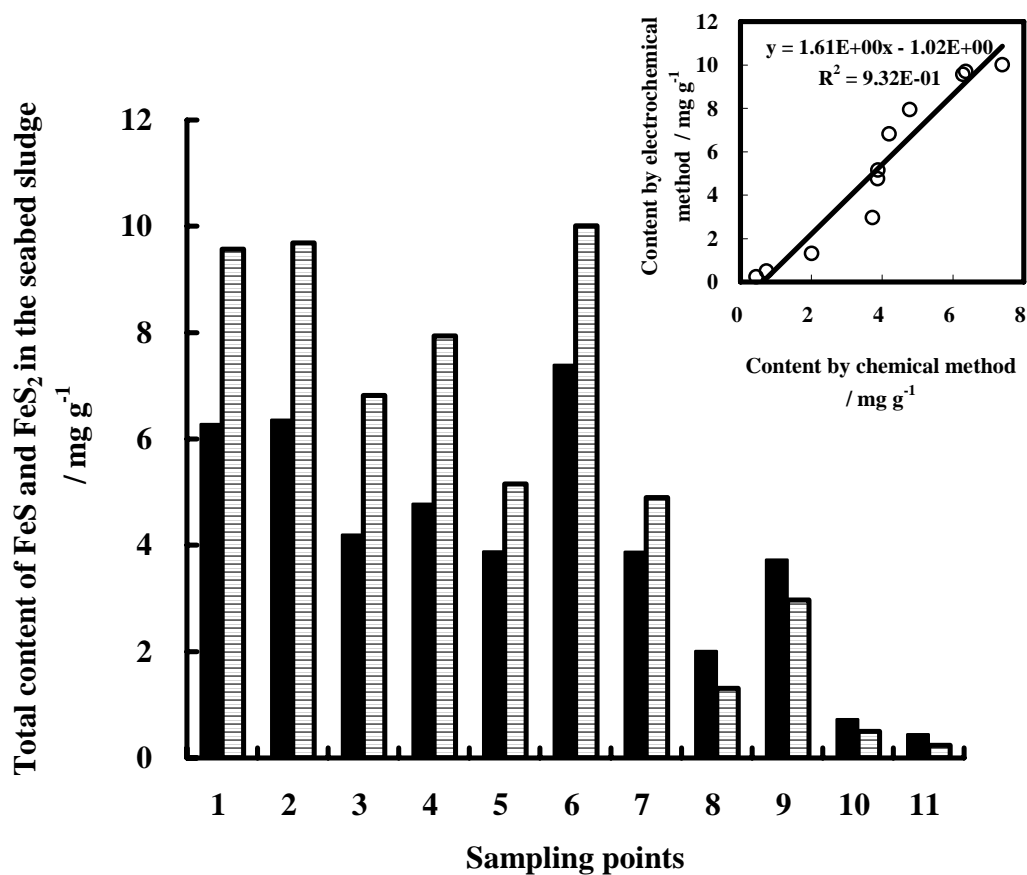
Figure 4.13 Determination of total content of iron(II) sulfide and iron disulfide in the solid

component of seabed sludge from Uranouchi Bay. (A) Measured content of FeS and FeS_2, respectively, by chemical method. Black column: the content of FeS_2; White column: the content of FeS. (B) Correlation between two methods for the measured total contents of FeS and FeS_2. Black column: by chemical method, corresponding to the total amount of FeS and FeS_2 as shown in Figure 4.13A; Strip column: by electrochemical method. The inserted picture shows the linear regression analysis for the correlation between both methods.

4.4 Conclusions

Iron(II) sulfide is an important reductive pollutant in the seabed sludge, the existence of which has harmful influence to the aqueous ecosystems, so that it is necessary to determine its content to protect the quality of water body. According to cyclic voltammetry, we found that after being electrolytically oxidized in twin electrode, slightly soluble iron sulfide can be transformed into soluble ferric ion. This makes it possible to determine the iron sulfide by electrochemical method. We investigated the influence of oxidation potential and oxidation time upon the generation of ferric ion from iron sulfide, and found potential of 2V (vs. SCE) for one minute of oxidation was suitable for the experiment.

There is a linear relation between the concentration of generated ferric ion and the iron sulfide weight percent in sludge. According to this linear relation, namely the *second calibration curve*, we can determine the iron sulfide weight percent from the concentration of ferric ion. Herein, the concentration of ferric ion can be measured by technique of chronoamperometry with twin electrode which was proposed in Chapter 2. On the other hand, the solid weight percent in the sludge can be evaluated by conductometry (see Chapter 3), namely, *the first calibration curve*. Therefore, a new electrochemical technique by twin electrode is developed, which including electrolysis, chronoamperometry and conductometry, for the assay of iron sulfide content in the solid component of seabed sludge. When the technique was applied to the artificial seabed sludge, the measured iron sulfide content agreed well with the reference value by preparation, indicating the feasibility of the proposed electrochemical.

However, when we applied the method to the real seabed sludge from Uranouchi Bay,

a deviation was found between the electrochemical method and chemical method. This is due to the existence of FeS_2, which is another type of iron sulfide and can also response to the proposed electrochemical method. After considering the contribution of FeS_2 to the measured total content of iron sulfide, we observed a good correlation between the electrochemical method and the chemical method.

CHAPTER 5

RAPID DETERMINATION OF IRON SULFIDE CONTENT IN THE SLUDGE OF LAKE BY ELECTROCHEMICAL METHODS WITH TWIN ELECTRODE

5.1 Introduction

Lake is a water body where water flows slowly. When industrial and domestic wastewater are discharged into a lake, via the action of anaerobic bacteria, some sulfate and sulfur organic substances from the wastewater are decomposed into sulfide ion. Similar to the case in a bay, when sulfide ion meets with ferrous ion, it follows the formation of iron sulfide, which finally precipitates to the bottom and accumulate in the sludge. As described in the previous chapter, since iron sulfide has harmful effect to the aquatic ecosystem, it is necessary to measure the content of iron sulfide in the lake sludge.

We have developed a new technique to determine the iron sulfide content in the sludge of sea by electrochemical methods with twin-electrode. For this technique, two calibration curves that we have established are essentially necessary, which consist of three important procedures, that is, conductometry, electrolysis and chronoamperometry. The first calibration curve corresponds to a linear relation between the conductivity ratio and solid fractional volume in a suspension ($\kappa/\kappa_0 = 1 + aV_f \ (0 \leq V_f < ca.0.25)$). According to this curve, the solid wt% can be determined by conductometry. The second calibration curve corresponds to the linear relation between FeS wt% and the concentration of ferric iron which was generated from the electrolysis of FeS ($[Fe^{3+}] = bFeSwt\%$). According to this curve, the FeS wt% can be evaluated from the determination of ferric ion by chronoamperometry.

Now, we intend to apply this technique to the determination of iron sulfide in the sludge of lake. However, the concentration of electrolyte in the lake is extremely low. This is disadvantageous to the flow of electric current which is necessary for an

electrochemical method. The solution to the problem is adding electrolyte to the sludge, but after addition of electrolyte, the concentration of electrolyte in the sludge sample will change. It is uncertain whether the change of electrolyte concentration in the sludge will affect the three important procedures (conductometry, electrolysis and chronoamperometry).

In this chapter, we report the effect of electrolyte on the technique for determination of iron sulfide content by electrochemical methods. Moreover, we attempt to propose a method that is suitable for the determination of iron sulfide content in the sludge of lake.

5.2 Experimental Section

5.2.1 Materials and Sample Preparation

Reagents of iron sulfide, SiO_2, $K_3[Fe(CN)_6]$, NaCl, KCl, LiCl and poly-vinylpyrrolidone (PVP) were purchased from Nacalai Tesque, INC. and were used without further purification. Deionized water prepared by Milli-Q (Millipore Corp.) was used for all aqueous solutions. Three kinds of 1-1 salts NaCl, KCl and LiCl were used to prepare electrolyte solutions. A concentrated KCl solution of 3.0 M was used as additional electrolyte to the freshwater sludge sample.

Artificial sludge samples were prepared by uniformly dispersing FeS-SiO_2mixture powder into a disperse medium. The reagents of FeS and SiO_2 have been crushed for 3 minutes before preparation for suspensions. The disperse medium was aqueous solution of poly-vinylpyrrolidone (PVP). Herein, PVP was used to achieve a viscosity sufficient of a disperse medium to prevent sedimentation of the dispersoids during the process of measurement, which had been introduced in the previous work (see Chapter 3).

5.2.2 Apparatus

Twin electrode was used as working electrodes in the electrochemical experiments. It was composed of two platinum plates purchased from Nilaco Co. and a Teflon spacer with thickness of 300μm. The effective area of twin electrode is 4cm^2 with a clearance of 300μm. For the structure of twin electrode in detail, it has been described in Chapter

2. A saturated calomel electrode (SCE) and a platinum wire ring were used as the reference and auxiliary electrodes, respectively. Dual Potentiostat, BAS Co., was used for chronoamperometry. The current of the working electrode was recorded with Digital recorder, Yokogawa, DL708.

We performed electrical conductivity measurement with MC126 conductivity meter (Mettler-Toledo) or Kohlrausch Bridge. For arrangement of the Kohlrausch Bridge, twin elecrode was used as electrolytic cell and the alternating current was obtained from Model 458A function generator (Kikusui Electronic Corp.). A Model LT364L oscillator was provided by Iwatsu Electric Co. LTD..

5.2.3 Electrochemical Method

The electrolysis experiment was performed with twin electrode at 2V for one minute. In carrying out the chronoamperometry for determination of $Fe(CN)_6^{3-/4-}$, the potential of electrode 1 was stepped from 0.4V to 0.0 V with keeping the electrode 2 at 0.4V (*vs.* SCE); for determination of $Fe^{3+/2+}$, potential step was carried out from 0.7V to 0.3V or electrode 1 when the potential of electrode 2 was held at 0.7V (*vs.* SCE). Before each experiment, the working electrode has been polished with $0.05\mu m$ alumina powder (BAS Co.) on a wet pad wetted with Milli-Q water. For all the processes of electrochemical experiments, the temperature of samples was controlled at 25°C.

5.2.4 Chemical Analytical Method

Chemical analytical method for determination of iron sulfide ($FeS+FeS_2$) in the wet sludge sample of lake was carried out by utilizing the chemical method for analysis of acid volatile sulfide (AVS) and chromium-reducible sulfur (CRS).[55-60] After addition of acid and reducing agents to the sediment sample, the produced H_2S was sparged with N_2 to a trapping solution, which was followed by the determination of sulfide in the trapping solution through iodimetric analysis. The amount of solid content in the wet sample was determined separately with dry-weight method.

5.2.5 Sludge Sampling

The real environmental freshwater sludge samples were taken by an Ekman dredge of 5141A (Rigosha & Co., Ltd,) from Kasumigaura lake in Ibaraki, Japan. The sampling locations were shown in Figure 5.1.

The samples were passed through a stainless steel sieve of 2.0 mm hole-size to remove lump of remains of organisms. All the samples were then deaerated with presaturated argon and kept in brown bottles. The process of pretreatment and storage of freshwater sludge were same as those of seabed sludge, which had been introduced in Chapter 3.
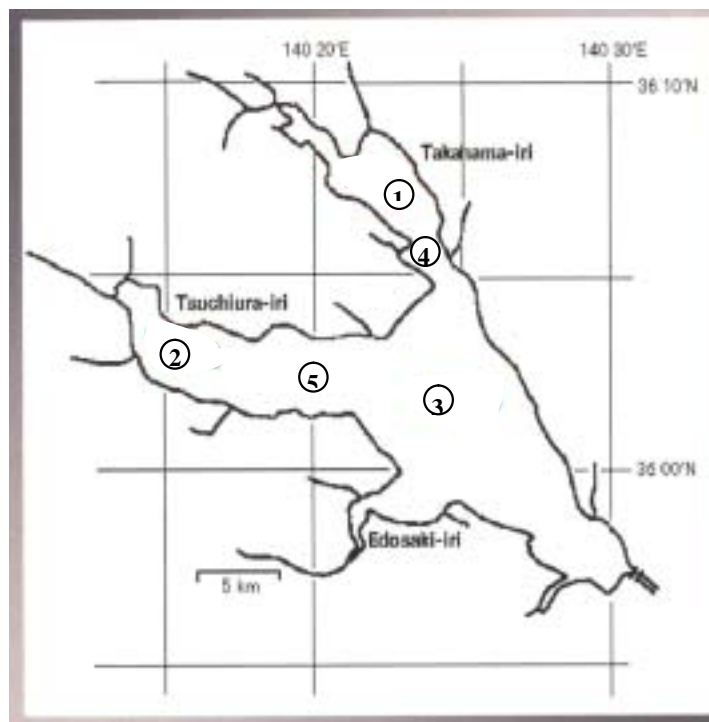
Figure 5.1 A map of Kasumigaura Lake of Ibaraki in Japan showing the sampling locations.

5.3 Results and Discussion

For lake sludge samples, it is necessary to add electrolyte to the sludge sample in order to perform electrochemical experiment. However, it is uncertain whether the two

calibration curves, which have been established to determine iron sulfide content in the sludge of sea, are still applicable to the lake sludge where electrolyte concentration is different from that in seabed sludge. For this reason, it requires to investigate the dependency of the two calibration curves on the concentration of electrolyte, that is, investigate the dependency of conductometry, electrolysis and chronoamperometry on the electrolyte concentration.

5.3.1 Dependency of the First Calibration Curve on the Electrolyte Solution

In Chapter 3, we proposed an empirical equation expressed by $\kappa/\kappa_0 = 1 + aV_f$, namely, the first calibration curve, to determine the solid content in a suspension by conductivity measurement. Herein, κ and κ_0 are the specific conductivity of the suspension and the disperse medium, respectively, and V_f is the solid fractional volume in the suspension. Parameter a is a constant that corresponds to the slope of the plot of conductivity ratio κ/κ_0 *vs.* V_f. In this chapter, we use different concentration of NaCl solutions as electrolytes with system of SiO_2 suspension containing PVP to study the effect of concentration of electrolyte on the conductometry. The experimental results are shown in Figure 5.2. As generally reported, [103] the electrical conductivity is dependent on the concentration of electrolyte, while as shown in Figure 5.2, the ratio of conductivity is independent of the concentration of electrolyte. The concentration of electrolyte varies from 0.05M to 0.50M, but the slopes of the plots of κ/κ_0 *vs.* V_f are almost same, indicating parameter a in the empirical equation is independent of the concentration of electrolyte. This means after adding electrolyte to the freshwater sludge sample, the first calibration curve is still applicable to the determination of solid wt% in the sludge by conductometry.
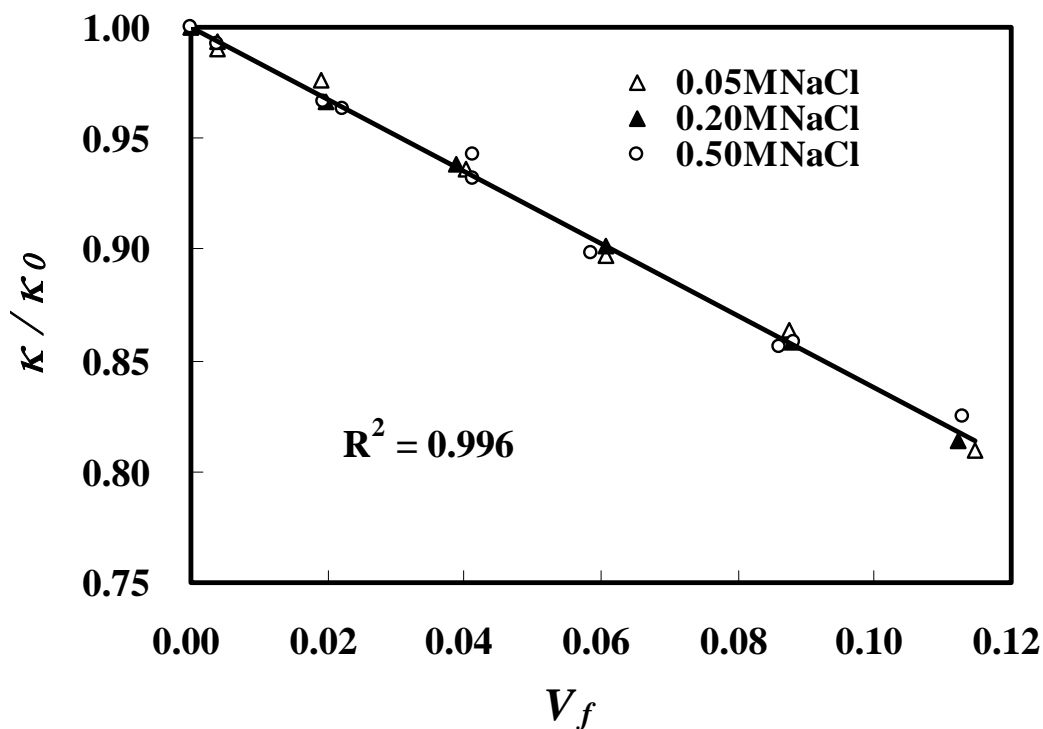
Figure 5.2 Dependency of the first calibration curve on the concentration of electrolyte solution for SiO_2-PVP suspension, with various concentration of NaCl solutions as electrolyte: (A) 0.05M; (B) 0.20M; (C) 0.5M.

5.3.2 Dependency of the Second Calibration Curve on the Electrolyte Solution

The second calibration curve is expressed by $[Fe^{3+}] = b$FeSwt%, where the $[Fe^{3+}]$ is the concentration of ferric ion from the electrolysis of FeS; and b denotes the slope of the linear relation between $[Fe^{3+}]$ and FeSwt%. As mentioned above, the second calibration curve was obtained through two steps of experiments: (1) electrolysis of FeS; and (2) the determination of concentration of ferric ion $[Fe^{3+}]$ by chronoamperometry. According to this, our investigation herein consists of two parts: (1) evaluation of dependency of chronoamperometry on the electrolyte solution; and (2) evaluation of dependency of electrolysis on the electrolyte solution.

Dependency of Chronoamperometry on the Electrolyte Solution. The evaluation of

the dependency of the chronoamperometry on the electrolyte solution was performed based on the results of determination of ferricyanide iron $Fe(CN)_6^{3-}$ by chronoamperometry, since $Fe(CN)_6^{3-}$ is one of the most commonly used electrochemical test species. We use 0.1M and 0.5M NaCl solutions as supporting electrolyte, respectively. The experimental results were shown in Figure 5.3. It was found that there was no difference in using either 0.1M or 0.5M NaCl solutions as electrolytes for the determination of $Fe(CN)_6^{3-}$ by chronoamperometry. The concentration of electrolyte solution varied, but the measured results showed almost same slopes for the linear relations between measured and prepared values of $Fe(CN)_6^{3-}$. This reveals that within our surveyed range, the chronoamperometry is undependent of the concentration of supporting electrolyte for the determination of electroactive substrate. This prediction is also supported by other researchers' studies. [109] The studies prove that for one-electron electrode reaction involving both reactant and product charged, the influence from the additional electrolyte upon the chronoamperometry technique can be neglected. According to the findings above, herein, it is reasonable to conclude that adding electrolyte has no effect on the determination of $[Fe^{3+}]$ by chronoamperometry within certain range of electrolyte level.
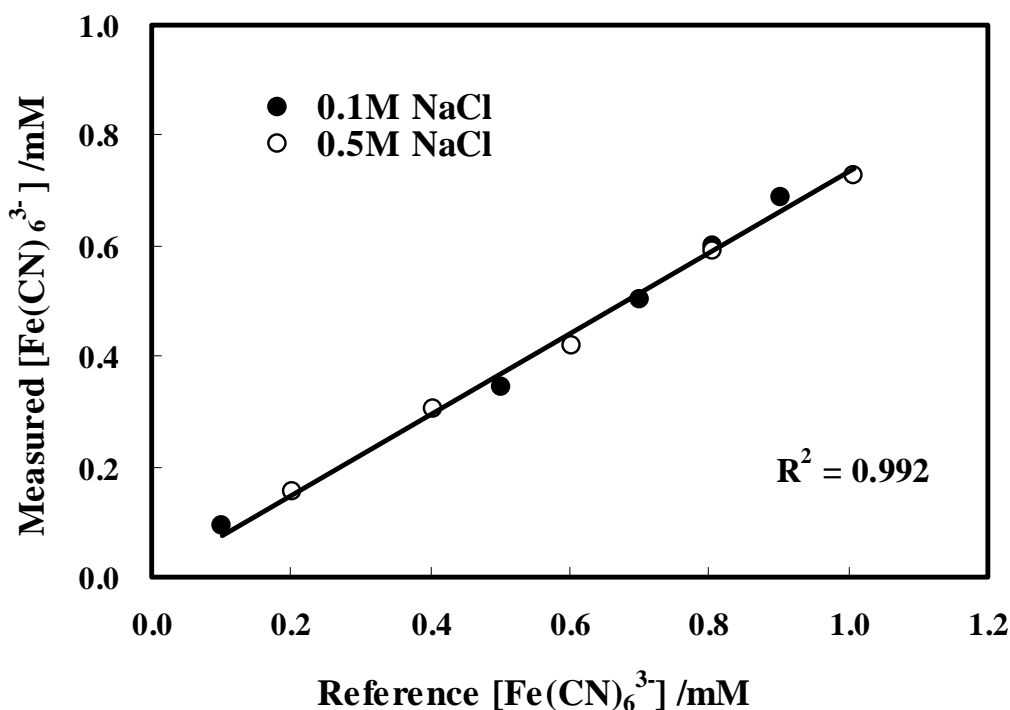
Figure 5.3 Effect of electrolyte concentration on determination of electroactive species by

chronoamperometry with different concentration of NaCl solutions as electrolytes: (A) 0.1M; (B) 0.50M.

Dependency of Electrolysis on the Electrolyte Solution. The determination of ferric ion by chronoamperometry is independent of the concentration of electrolyte solution, but we found that the slope of the second calibration curve changes with the concentration of NaCl electrolyte solution as shown in Figure 5.4A. This means the process of electrolysis of iron sulfide depends on the concentration of electrolyte solution. With the increasing of concentration of electrolyte solution, the slopes of the calibration curves increase, that is, the coefficient *b* in expression $[Fe^{3+}] = b$FeSwt% varies with the increasing of concentration of the electrolyte solution. When we use other 1:1 salts, such as KCl or LiCl as electrolyte, similar situations were observed (see Figures 5.4B and 5.4C), suggesting that coefficient *b* is dependent on the concentration of electrolyte solution.
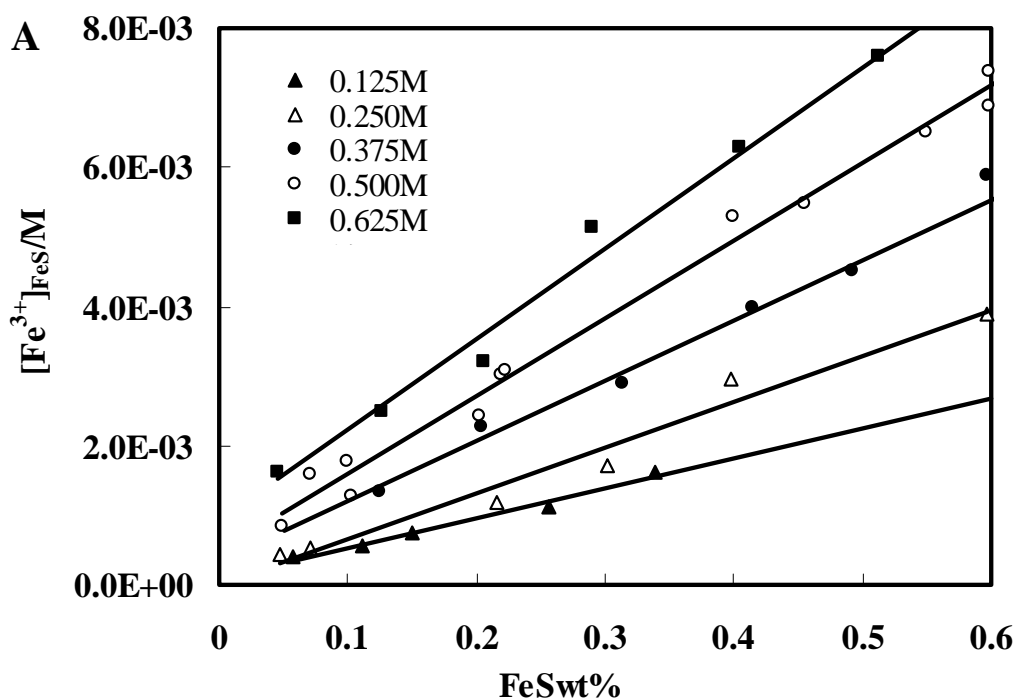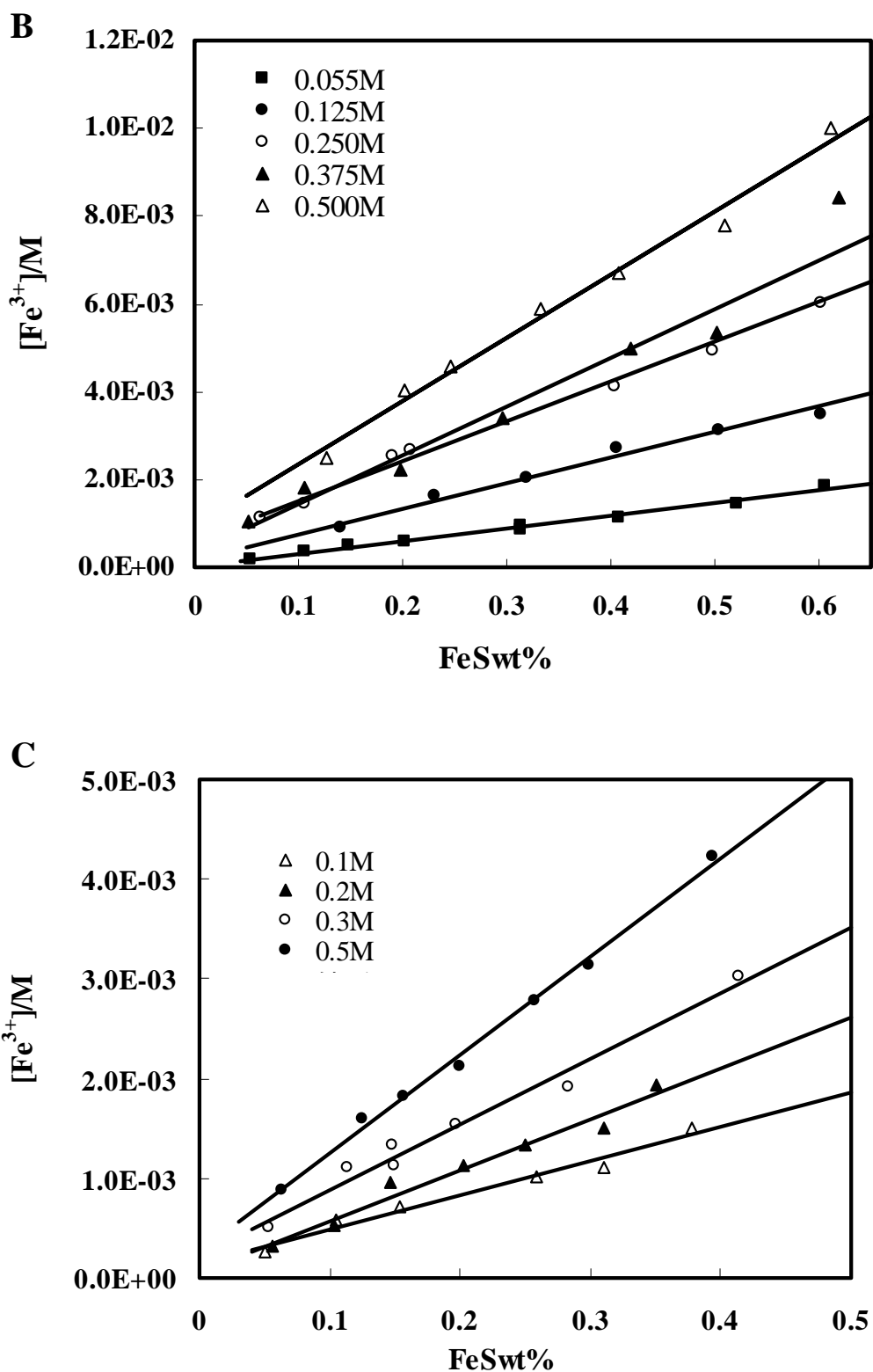
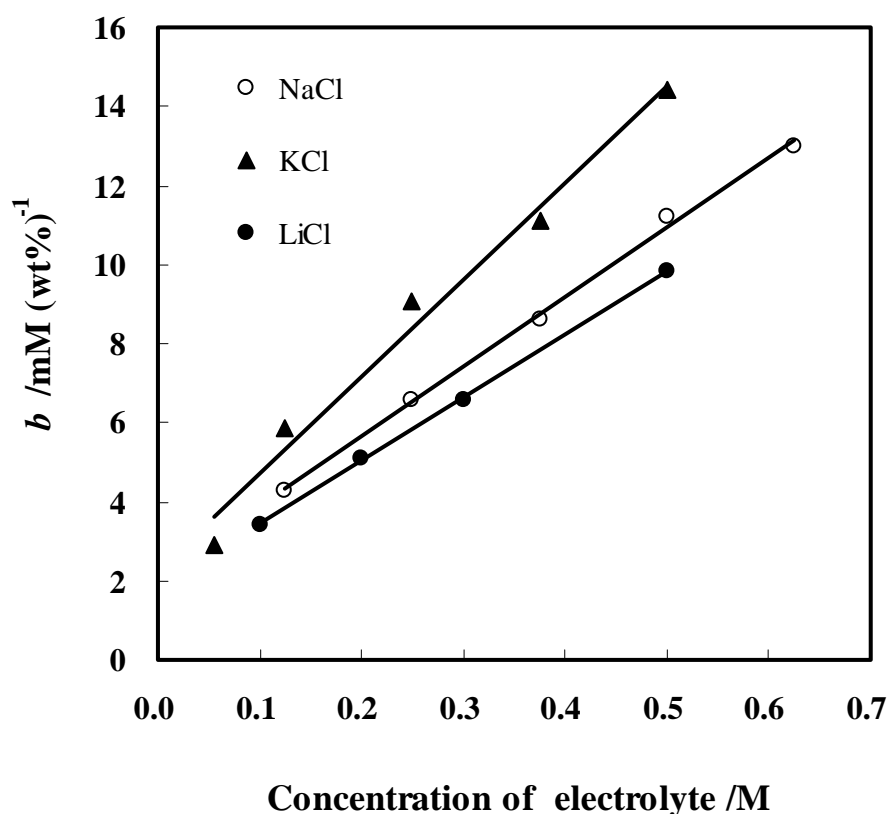**Figure 5.4** Dependency of coefficient b of the second calibration curve $[Fe^{3+}] = b$FeSwt% on the concentration of various electrolyte solutions: (A) NaCl solution; (B) KCl solution;

(C) LiCl solution.

For a given kind of electrolyte, the coefficient b is directly proportional to the concentration of electrolyte solution, which is shown in Figures 5.5. It seems that we can determine the coefficient b on the basis of the concentration of electrolyte solution in the sample. However, for different kinds of electrolytes, the slope of the linear relation between b and concentration of electrolyte solution is quite different. It is possible to define the kind and the amount of the added electrolyte, but for different suspension sludge sample, the original water contents is different, so that it is in fact difficult to exactly and rapidly determine the concentration of electrolyte in the sludge samples after addition of the electrolyte. It follows the result that it is impracticable to evaluate the value of coefficient b solely on the basis of the concentration of electrolyte in the sludge.

Figure 5.5 Dependency of the coefficient b on the concentration and the type of electrolyte solution with NaCl, KCl and LiCl as electrolyte, respectively.

However, we found that the coefficient *b* of the second calibration curve is proportional to the specific electrical conductivity of disperse medium, κ_0, irrespective of the kind and the concentration of electrolyte of 1:1 salt (see Figure 5.6). Three kinds of electrolytes with various concentrations, including NaCl, KCl and LiCl, were investigated on the relation between the coefficient *b* and the electrical conductivity of the disperse medium. We found a good linear relation between *b* and κ_0. As is shown in Figure 5.6, when using seawater as electrolyte, the result also consisted with this linear relation. This indicates that it is reasonable to regard this linear relation as a calibration curve. According to the linear relation, we can readily evaluate the coefficient *b* from the determination of conductivity of the disperse medium, irrespective of the kind and the concentration of the electrolyte in the sludge.
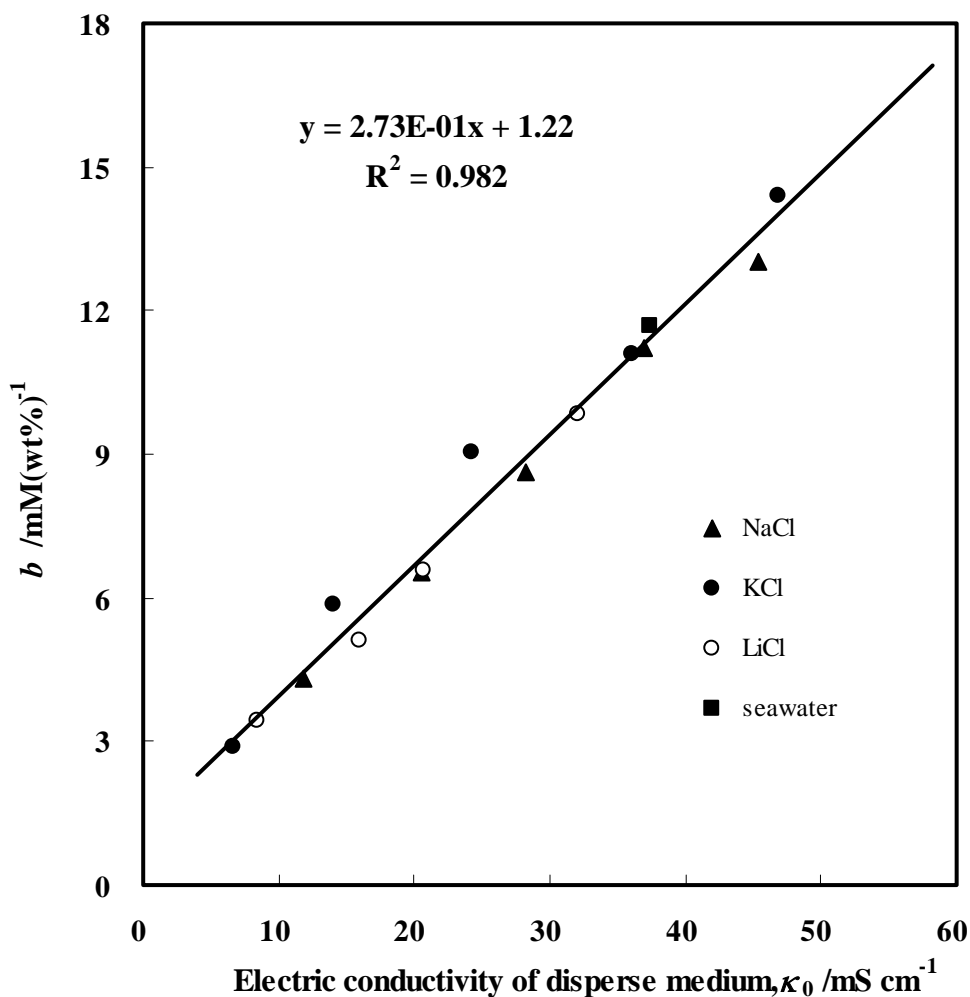
Figure 5.6 Dependency of the coefficient *b* on the electrical conductivity of the disperse medium with various electrolyte solutions.

5.3.3 A Method for Determination of Iron Sulfide Content in the Freshwater Sludge

According to the findings above, we can propose a method for the determination of FeS content in the freshwater sludge, which was described as follows: Certain amount of electrolyte solution is first being added to the freshwater sludge sample. Herein, we use 3M KCl solution as added electrolyte. Then the conductivity of sludge suspension is determined, expressed as κ. Furthermore, the electrolysis of FeS in the sludge is performed at 2V for one minute. During this process, slightly soluble iron sulfide can be converted to soluble ferric ion. In this case, we can determine the concentration of ferric ion by chronoamperometry. Next, the sludge sample is filtered, following the measurement of conductivity of filtrate, expressed by κ_0. Based on the value of κ_0, we can evaluate the coefficient b of the second calibration curve. The following procedures are same as that for seabed sludge sample, that is: (1) According to the values of κ_0 and κ, we evaluate the solid wt% in the sludge on the basis of the first calibration curve; (2) According to the value of ferric ion concentration and the second calibration curve, we evaluate the FeS wt%; (3) We can finally determine the FeS content in the solid component of the sludge sample based on the ratio of FeS wt% and solid wt%. Therefore, a method for determination of iron sulfide in the freshwater water sludge is developed.

5.3.4 Determination of Iron Sulfide Content in the Artificial Freshwater Sludge Samples

The applicability of the proposed method was validated using the artificial freshwater sludge samples, which were prepared by dispersing powder of FeS-SiO$_2$ mixture into the PVP aqueous solution. Figure 5.7 showed the correlation between the measured value by electrochemical method and the known value by preparation. Herein, the values of FeS content (%) at x-axis and y-axis represent the ratio of FeS content over the total amount of FeS-SiO$_2$ mixture, expressed as weight percent. We found a good agreement between the two sets of values of FeS content, as demonstrated by the high significant correlation $R^2 = 0.981$ and the slope of 0.998. This indicates that the

proposed method is valid for the determination of FeS content in the freshwater sludge samples.
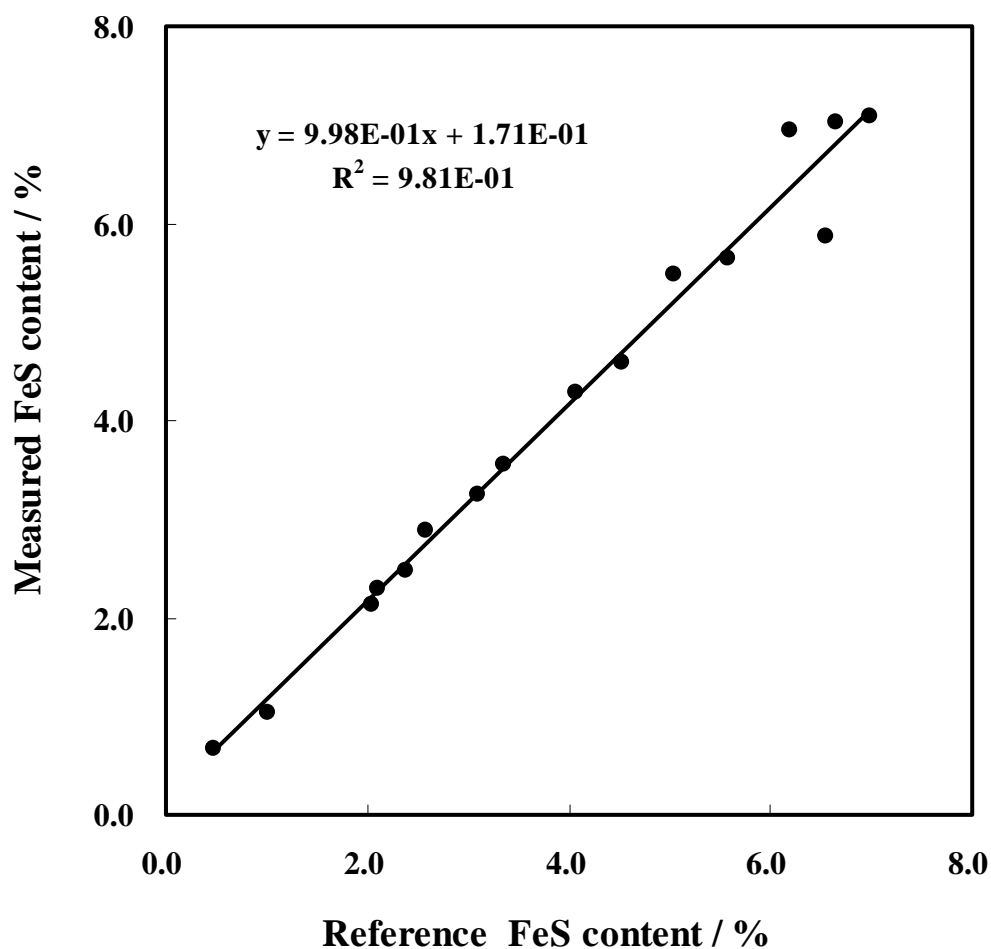
Figure 5.7 Correlation between the value measured by electrochemical method and the reference value by preparation for FeS content in the artificial freshwater sludge samples.

5.3.5 Correlation between by Conductivity Meter and by Twin Electrode Cell for the Determination of Specific Electrical Conductivity of the Aqueous and Suspension Samples

We have developed a technique to determine the iron sulfide content in the freshwater sludge by electrochemical method including conductivity measurement, electrolysis and chronoamperometry. For electrolysis and chronoamperometry, both of

them were performed in the same twin electrode cell, whereas for conductivity measurement, it was carried out by conductivity meter. This means that it requires additional conductivity meter except for twin electrode cell to perform the whole determination of this technique. This is inconvenient to achieve in situ measurement, so that we need to study the possibility of measurement of electrical conductivity by twin electrode. If it is successful, the whole experiments for determination of iron sulfide can be performed in the same twin electrode.

For sample of KCl aqueous solutions, the relation between by meter and by twin electrode for the conductivity measurement was shown in Figure 5.8. As can be seen, the relation is a curve, rather than a straight line. With the increasing of conductivity value, the slope of the curve increases. This might be due to the small clearance of only 300μm between the twin electrode, whereas the common distance for conductivity measurement is 10^4 μm.[2] The small distance may lead to relatively stronger electrical double-layer effect [110] for conductivity measurement, so that twin electrode gave an underestimation of the conductivity value comparing with conductivity meter. For the same sample, the measured values increase with the increasing of distance between twin electrode.

However, according to the relation curve in Figure 5.8, the measured value by twin electrode can be calibrated to the corresponding one by meter which is regarded as the correct value. Thus, the correct value of conductivity can be obtained based on the result measured by twin electrode cell. That means we can perform the whole procedure with only twin electrode cell for the determination of iron sulfide content in the freshwater sludge. However, it is worthy to note that in order to keep the stability of measurement, the twin electrode should be calibrated by a standard solution with known conductivity value before a conductivity measurement. For example, for the relation curve in Figure 5.8, aqueous solution of 0.07M KCl with 8.26 mS/cm was used as a standard solution. All the other measured values have been corrected according to this value.

$$y = 3.26E\text{-}04x^4 - 1.23E\text{-}02x^3 + 1.81E\text{-}01x^2 + 1.50E\text{-}01x$$
$$R^2 = 9.99E\text{-}01$$
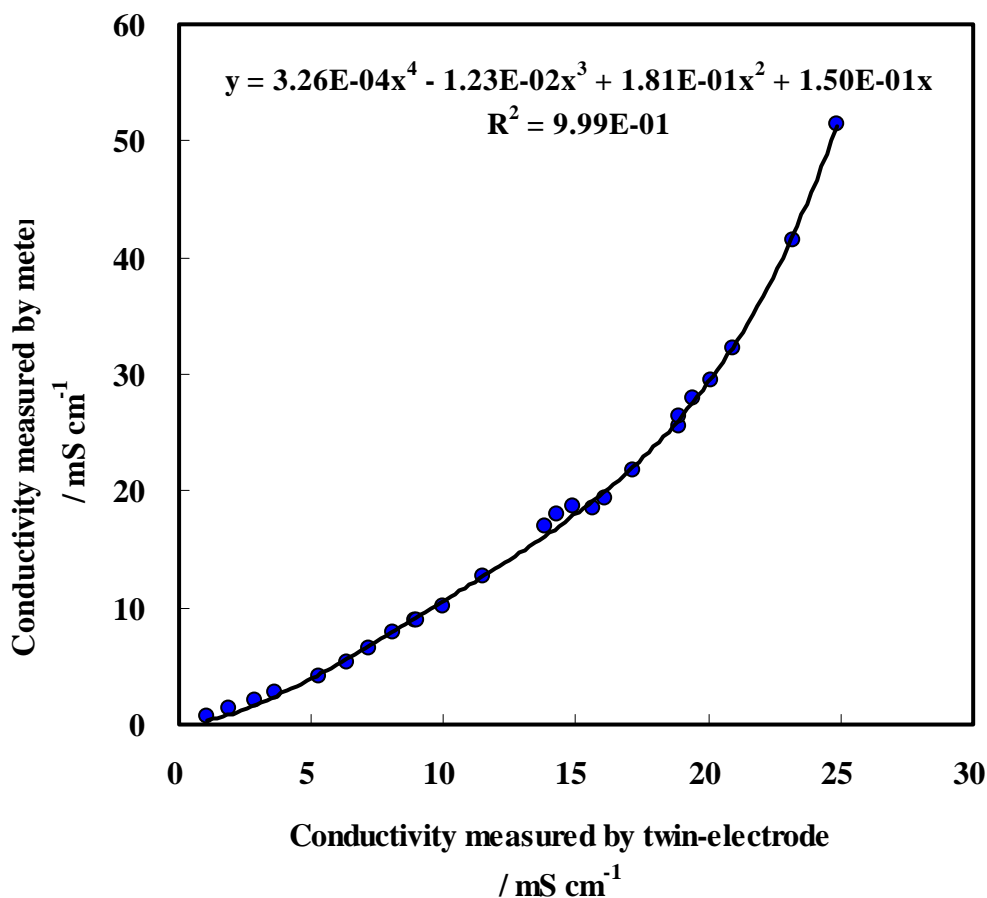
Figure 5.8 Correlation between by conductivity meter and by twin electrode cell for determination of specific electrical conductivity, using KCl aqueous solution as sample.

5.3.6 Determination of FeS Content in the Artificial Freshwater Sludge by only Twin Electrod

According to the calibration curve in Figure 5.8, we can determine the conductivity with twin electrode, so that it is possible to determine the iron sulfide content in the freshwater sludge with only twin electrode cell. We applied it to the measurement of iron sulfide content in the artificial sludge samples of freshwater. The results were shown in Figure 5.9. The values in the x-axis and y-axis have the same meanings as previously shown in Figure 5.7. As can be seen in Figure 5.9, a good agreement was obtained with slope of 1.10 and $R^2=0.94$ between the measured value and prepared value, demonstrating that it was feasible using only twin electrode cell to determine the

iron sulfide content in the freshwater sludge.
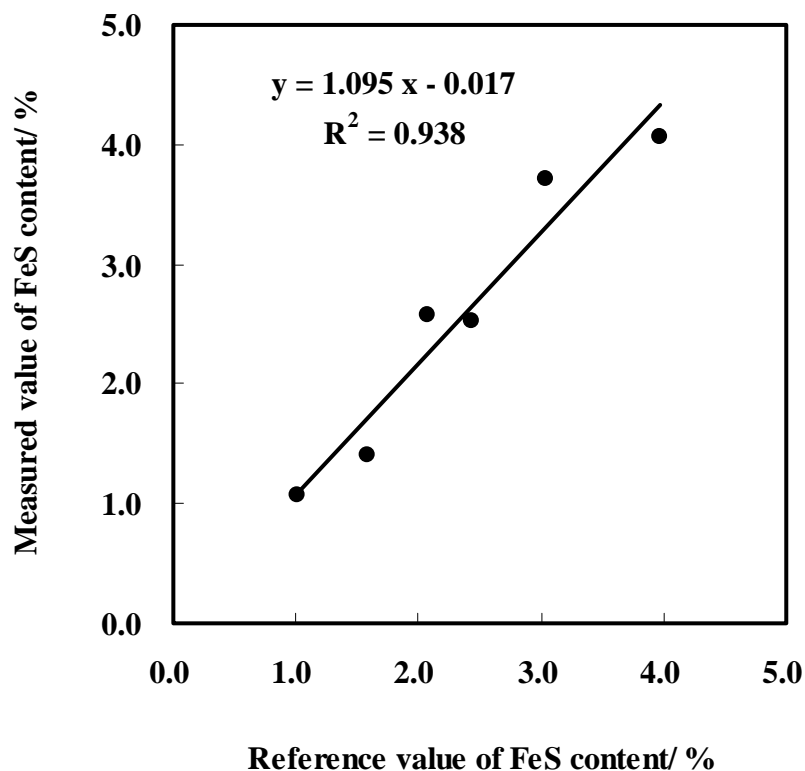
Figure 5.9 Iron sulfide content in the artificial freshwater sludge by twin electrode

5.3.7. *Determination of Iron Sulfide Content in the Real Freshwater Sludge of Kasumigaura Lake*

To validate the proposed method further, the determination of iron sulfide content in the real freshwater sludge was carried out. These real sludge samples were collected from the Kasumigaura Lake (see Figure 5.1) and were analyzed by three methods, including conventional chemical extraction method, electrochemical method by twin electrode and additional conductivity meter, as well as electrochemical method by only twin electrode, respectively. The correlations among them were given in Figure 5.10. Herein, the content of iron sulfide includes total amount of FeS and FeS_2. A good agreement of the measured results was obtained as shown in Figure 5.10A. A highly significant correlations ($R^2 = 0.974$ in Figure 5.10B, and $R^2 = 0.954$ in Figure 5.10C) between the conventional chemical method and the electrochemical method indicated

that the two kinds of methods agreed well. More importantly, the slopes of 1.02 and 0.938 were observed. Considered that there are analytical errors associated with both the electrochemical method and the conventional chemical extraction method, as well as usually it is difficult to analyze the pollutant in the heterogeneous sludge sample, the strong correlations and the slopes obtained provided compelling support for the suitability of the proposed electrochemical method for measuring iron sulfide content in the freshwater sludge sample. Although the accuracy of technique by only twin electrode (see Figure 5.10C) is a little bit less than that by twin electrode with additional meter (see Figure 5.10B), it is advantageous to achieve the on site measurement with only twin electrode cell without additional conductivity meter. Regarding this point, the technique with only twin electrode cell is preferable to be employed to determine iron sulfide content in the lake sludge.

It is worthy to note that by far we can not separately determine the amount of FeS and FeS_2 by electrochemical method, since both of FeS and FeS_2 respond to the electrochemical signal, and together contribute to the total amount of iron sulfide. Thus, the measured values by the electrochemical method indeed include the amount of FeS and FeS_2, being expressed as FeS content. This may lead to some deviation from true value. In addition, even for conventional chemical method for determination of FeS and FeS_2, it is still difficult to achieve 100% recovery, so that the chemical mehtod will give an underestimate to the measurement. All of these factors may contribute to the deviation between the measured values by conventional chemical method and by electrochemical method.

A

Iron sulfide content in solid component of the sludge/ mg g^{-1} (y-axis)

Sampling points (x-axis): 1, 2, 3, 4, 5

■ Chemical analytical method (FeS)
□ Chemical analytical method (FeS$_2$)
■ Electrochemical method by twin electrode and meter
▨ Electrochmical method by twin electrode

B

$y = 1.02E+00x + 1.03E+00$

$R^2 = 9.74E-01$

Iron sulfide content measured by electrochmical method with twin electrode and meter/ mg g^{-1}

Iron sulfide content measured by chemical analytical method/ mg g^{-1}

C

$y = 9.38E-01x + 1.29E+00$

$R^2 = 9.54E-01$

Iron sulfide content measured by electrochmical method with twin electrode/ mg g^{-1}

Iron sulfide content measured by chemical analytical method/ mg g^{-1}

Figure 5.10 Measurement results of iron sulfide content in the real freshwater sludge samples from Kasumigaura Lake. (A) Comparisons among by conventional chemical extraction method, by electrochemical method with both twin electrode and conductivity meter, and by electrochemical method with only twin electrode. (B) Correlation between the result by electrochemical method with both twin electrode and meter and that by

conventional chemical extraction method. (C) Correlation between the result by electrochemical method with only twin electrode and that by conventional chemical extraction method.

5.4 Conclusions

The concentration of electrolyte in the lake is extremely low. This is disadvantageous to the flow of electric current which is necessary for an electrochemical method. It is necessary to add electrolyte in order to apply the electrochemical technique to the lake sludge sample.

We investigated the effect of adding electrolyte on the determination of iron sulfide content in the sludge by electrochemical method. It was found that the conductivity ratio was independent of the concentration of electrolyte in the sludge, indicating that after adding electrolyte to the sludge sample, the first calibration curve was still applicable to the determination of solid wt% by conductometry. Furthermore, we found that adding electrolyte had little effect on the chronoamperometry itself for determination of ferric ion within the surveyed range of electrolyte level. More important, we found that the electrolysis rate of the iron sulfide was directly proportional to the specific electrical conductivity of the disperse medium, κ_0, rather than the concentration of electrolyte. This relation is essential useful, because we can evaluate the coefficient b of the second calibration curve rapidly from κ_0. Therefore, we proposed a method for determination of iron sulfide content in the sludge of lake. When applying this method to the artificial and real freshwater sludge of freshwater, we observed good agreements between the measured results and the reference values.

Moreover, we found a relationship of conductivity measurement by meter and twin electrode. According to this relation curve, it is possible to evaluate the true value of κ_0 by twin electrode. Thus, we can perform the whole determination of iron sulfide content in the sludge of lake by only twin electrode. We found that the measurement of FeS content by only twin electrode cell agreed well with those by conventional chemical method. This provided powerful support to the achievement of on site measurement of FeS content in the freshwater sludge by electrochemical method.

CHAPTER 6

CONCLUSIONS

This thesis mainly deals with the development of a rapid determination of iron sulfide content in the sludge of bay and lake by electrochemical method with twin electrode. The results obtained through this work are summarized as follows:

6.1 Summary and Conclusions

Iron sulfide is an important reductive pollutant in the sludge of sea and lake, but the conventional chemical method for its determination has several disadvantages, such as complicated procedure and time-consuming. In this thesis, we propose a new technique which rapidly determines the iron sulfide content in the seabed sludge by electrochemical methods with twin electrode, including conductometry, electrolysis and chronoamperometry, as shown in Figure 6.1. According to the first calibration curve $\kappa/\kappa_0 = 1 + aV_f$ $(0 \leq V_f < ca.0.25)$, a linear relation between the conductivity ratio and solid fractional volume in a suspension, which has been described in Chapter 3, we can rapidly evaluate the solid wt% in the suspension by conductometry. On the other hand, by electrolysis at 2V (*vs.* SCE) for 1 minute, the slightly soluble iron sulfide is transformed into soluble ferric ion. We have proposed a novel technique, as described in Chapter 2, which can simultaneously determine diffusion coefficient, concentration and oxidant mole fraction of reversible electrochemical active species by chronoamperometry in twin electrode. This is also the technique base for determining ferric iron by electrochemical method with twin electrode. Based on the second calibration curve that is described in Chapter 4, we determine the iron sulfide weight percent in the sludge. Finally, the iron sulfide content in the solid component of the seabed sludge can be evaluated on the basis of solid wt% and FeS wt%.
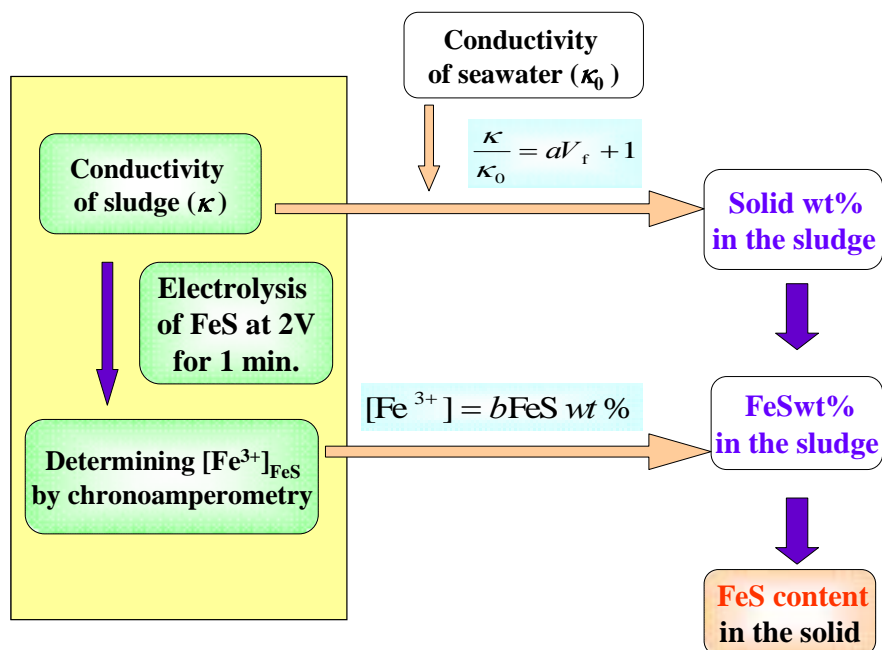
Figure 6.1 Determination of iron sulfide content in the sludge of sea**.**

After being modified, this technique can be also applied to the determination of iron sulfide in the sludge of freshwater, such as lake (see Figure 6.2). In general, the concentration of electrolyte in the lake is extremely low. This is disadvantageous to the flow of electric current which is necessary for an electrochemical method. The solution to the problem is adding electrolyte to the sludge. It is found that conductometry and chronoamperometry are independent of the addition of electrolyte to the sludge sample, whereas the electrolysis of iron sulfide is dependent on the electrical conductivity of disperse medium, κ_0, irrespective of the type of 1-1 electrolyte. There is a linear relation between the coefficient b of the second calibration curve and the conductivity of disperse medium, so that it is possible to evaluate the coefficient b from the determination of conductivity of disperse medium after addition of electrolyte to the sludge. Based on these findings, we propose a method for measurement of iron sulfide content in the sludge of lake. When applying this method to the artificial and real freshwater sludge of freshwater, we have obtained good agreements between the measured results and the reference values.
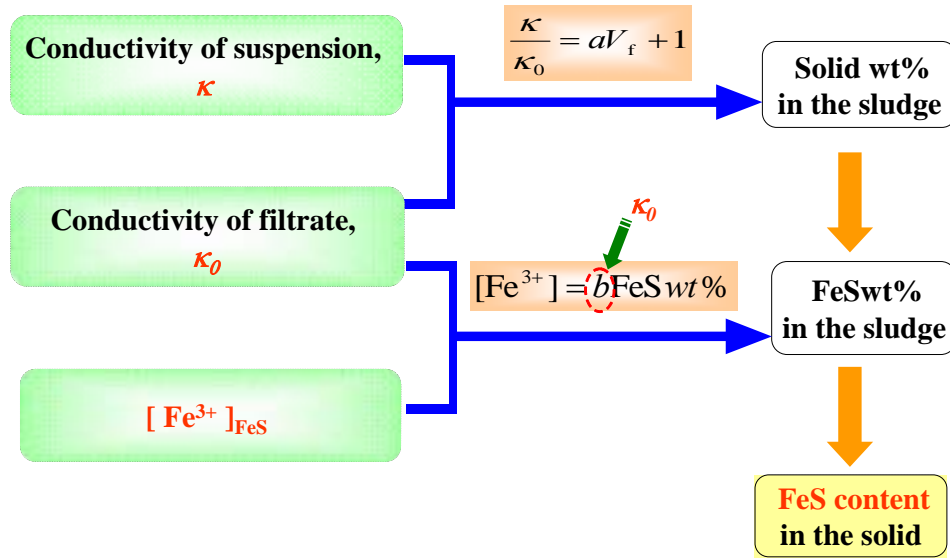
Figure 6.2 Determination of iron sulfide content in the sludge of lake.

In studying the possibility of determining electrical conductivity by twin electrode, we found that there was a deviation of the measurement result compared with the true value due to the narrow distance between twin electrode, but with the calibration curve estabilshed in Chapter 5, we can correct the underestimated value from twin electrode to the standard one. The experimental results proved that it was practicable using only twin electrode cell to perform the whole determination of iron sulfide. This is essentially useful to the achievement of on site measurement of iron sulfide content in the environmental sludge by electrochemical method.

The results mentioned above gave valuable information for the design and construction of instrument for on site measurement of iron sulfide content in the sludge of bay and lake. The author wishes that this thesis contributes to the environmental monitoring and the protection of aquatic ecosystem.

6.2 Suggestions for the future research

- An empirical equation, on the relation between conductivity ratio and solid content in a suspension, is proposed in Chapter 3, but the behaviors of the conductive

dispersoids in the suspension is not clearly yet, which needs more systematic studies

- There are some deviations of the results between the electrochemical method and the conventional chemical method for the determination of total iron sulfide ($FeS+FeS_2$). In order to eliminate the deviations, more study should be made on how to separately determine FeS and FeS_2 by electrochemical method, as well as how to achieve the 100% recovery of chemical method for determination of iron sulfide.

- Electrical conductivity is dependent on the temperature of sample measured, so that it requires to consider the temperature compensation when applying the technique to the on site measurement of iron sulfide in the bottom sludge of sea and lake, especially in the case of freshwater sludge where it is necessary to determine the exact value of κ_0. It is recommended to convert the value of conductivity measured at actual temperature into the value for conductivity at 25°C. According to Japanese Industrial Standards (JIS Standard), for simplicity, conversion is made with an assumption of a 2% variation in conductivity per °C, which is illustrated as the following formula:

$$\kappa_{25} = \frac{\kappa_t}{\{1+0.02\times(t-25)\}} \tag{7.1}$$

where t (°C) is the actual temperature; κ_{25} and κ_t are the conductivity at 25 °C and t °C, respectively. However, it needs to study more about this issue to confirm the assumption.

- After applying the proposed technique to the on site measurement of iron sulfide, the next research has to be carried out on how to remove/ utilize the settled iron sulfide from the bottom sludge of sea and lake.

REFERENCE AND NOTES

1. Fitzpatrick. J. A., Facettti, J. F. *Water, Air Soil Pollut.* **1981**, 15, 169-72.

2. Antonio M., Environmental Pollution Research in South America. *Environ. Sci. Technol.,* **1991**, 25(4), 590-594.

3. R. E. Hester and Roy M., *Chemistry in the Marine Environment*. Royal Society of Chemistry: Cambridge. **2000**.

4. Dwight B., *Environ. Sci. Technol.* **1967**, 1(8), 612-616.

5. Samuel J., *Environ. Sci. Technol.* **1970**, 4(3), 204-209.

6. Stan Miller, Carol Lewicke, *Environ. Sci. Technol.* **1972**, 6(12), 974-979.

7. Maldonado, C.; Dachs, J.; Bayona, J. M.; *Environ. Sci. Technol.;* **(Article); 1999**; 33(19); 3290-3296.

8. Donald C. M., *Environ. Sci. Technol.*, **1980**, 14(1), 32-37.

9. Robert Sperr Weston; *Ind. Eng. Chem.,* **1939**, 31(11), 1311-1315.

10. Milan J. Schwuger., *Detergents in the Environment*. (Surfactant Science Series. Volume 65) Marcel Dekker: New York, **1996**.

11. James C. S. Lu, Kenneth Y. Chen; *Environ. Sci. Technol.;* **1977**; 11(2); 174-182.

12. Ian W. C., Andrew B. C.; *Environ. Sci. Technol.;* **1995**; 29(5); 1288-1296.

13. Jackson, T. A.; West, M. M.; Leppard, G. G.; *Environ. Sci. Technol.;* **1999**; 33(21); 3795-3801.

14. A.; Ekelund, R.; Berggren, M.; Brorstrom-Lunden, E.; Bergqvist, P. A.; *Environ. Sci. Technol.;* **2000**; 34(16); 3323-3329.

15. Horne, R. A., "Marine Chemistry", Wiley-Interscience, New York, N.Y., **1969.**

16. Simpson, S. L.; Apte, S. C.; Batley, G. E.; *Environ. Sci. Technol.;* **1998**; 32(5); 620-625.

17. Foster-Smith, R. L. *J. Exp. Mar. Biol. Ecol.* **1978**, 32, 73-95.

18. Hirst, J. M.; Aston, S. R. *Estuarine Coastal Shelf Sci.* **1983**, 16, 549-558.

19. Prause, B.; Rehm, E.; Schulz-Baldes, M. *Environ. Technol. Lett.* **1985**, 6, 261-266.

20. Peterson, G. S.; Ankley, G. T.; Leonard, E. N. *Environ. Toxicol. Chem.* **1996**, 15, 2147-2155.

21. Morse, J. W. In *Metal Contaminated Aquatic Sediments*; Allen, H. E., Ed.; Ann Arbor Press: Ann Arbor, MI, **1995**; Chapter 8, pp 187-199.

22. James C. S. Lu, Kenneth Y. Chen; *Environ. Sci. Technol.;* **1977**; 11(2); 174-182.

23. Wakeman, T. H., "Mobilization of Heavy Metals from Resuspended, Sediments", 168th Meeting, ACS, Atlantic City, N.J., **1974**.

24. Calmano, W.; Forstner, U.; Hong, J. In *Environmental Geochemistry of Sulfide Oxidation*; Alpers, C. N., Blowes, D. W., Eds.; American Chemical Society: Washington, DC, **1994**; pp 298-321.

25. Howarth, R. W.; Giblin, A.; Gale, J.; Peterson, B. J.; Luther, G. W., *Ecological Bulletins*, **1983**, 35, 135-52.

26. Giblin, A. E.; Likens, Gene E.; White, D.; Howarth, R. W., *Limnology and Oceanography*, **1990**, 35(4), 852-69.

27. Joregensen B. B., *Nature*, **1982**, 296, 643-645.

28. Peterson, Bruce J.; Howarth, Robert W., *Limnology and Oceanography*, **1987**, 32(6), 1195-213.

29. Howarth, Robert W.; Sharpley, Andrew; Walker, Dan. *Estuaries*, **2002**, 25(4B), 656-676.

30. Emerson, S.; Jacobs, L.; Tebo, B. In *Trace Metals in Sea Water*; Wong, C. S., et al., Eds. Plenum Press: New York, **1983**.

31. Dyrssen, D.; Kremling, K. *Mar. Chem.* **1990**, *30*, 193-204.

32. Luther, George W., III; Church, Thomas M.; Giblin, Anne E.; Howarth, Robert W., *ACS Symposium Series*, **1986**, 305, 340-55.

33. Howarth, Robert W.; Joergensen, Bo Barker, *Geochimica et Cosmochimica Acta*, **1984**, 48(9), 1807-18.

34. Berner R. A., Am. Assoc. Pet. Geol., Mem. **1974**, 20, 524-531.

35. Berner R. A., Geochim. Cosmochim. Acta, **1984**, 48, 605-615.

36. Peterson, B. J.; Steudler, P. A.; Howarth, R. W.; Friedlander, A. I.; Juers, D.; Bowles, F. P., *Ecological Bulletins,***1983**, 35, 153-165.

37. Howarth, Robert W.; Giblin, Anne, *Limnology and Oceanography*, **1983**, 28(1), 70-82.

38. Howarth, Robert W, *Science* (Washington, DC, United States), **1979**, 203(4375), 49-51.

39. Georg S. *The Essential Guide to Environmental Chemistry*. Translated by Brooks H. John Wiley & Sons. **2001**.

40. R. J. G. Mortimer, J. T. Davey, M. D. Krom, P. G. Watson, P. E. Frickers and R. J. Clifton, *Estuarine, Coastal and Shelf Science*, **1999**, 48, 683-699.

41. Stephen R. Carpenter, David L. C., Jonathan J. C., Kathryn L. C., Xi He, James R. Hodgson, James F. K., Susan E. K., Michael L. P., et al.; *Environ. Sci. Technol.;* **1995**; *29*(3); 784-786.

42. Pretty, J. N.; Mason, C. F.; Nedwell, D. B.; Hine, R. E.; Leaf, S.; Dils, R.; *Environ. Sci. Technol.;* **2003**; *37*(2); 201-208.

43. Lamers, L. P. M.; Tomassen, H. B. M.; Roelofs, J. G. M.; *Environ. Sci. Technol.;* **1998**; *32*(2); 199-205.

44. Krom, M. D., R. A. Berner, *Geochim. Cosmochim. Acta*, **1981**, 45, 207-216.

45. McManus J., W. M. Berelson, K. H. Coale, K. S. Johnson, T. E. Kilgore, *Geochim. Cosmochim. Acta*, **1997**, 61, 2891-2902.

46. Anschutz, P., S. Zhong, B. Sundby. *Limnol. Oceanogr.* **1998**, 43, 53-64.

47. Slomp C. P., E. H. Epping, W. Helden, W. V. Raaphorst. *J. Mar. Res.*, **1996**, 54, 1179-1205.

48. Gunnars A., S. Blomqvist, *Biogeochemistry*, **1997**, 37, 203-226.

49. Goldhaber M. B. and Kaplan I. R., *The Sea*, (ed. E. D. Goldberg). Wiley. **1974**, 5, 569-655.

50. Berner R. A., Principles of Sediment Geochemistry. McGray-Hill, New York, **1971**.

51. W. Stummn, J. J. Morgan, *Aquatic Chemistry*. John Wiley & Sons, Brisbane, **1981**, 2nd ed.

52. Howarth, R. W.; Stewart, J. W. B., *SCOPE*, **1992**, 48, 67-84.

53. Austin, Amy T.; Howarth, Robert W.; Baron, Jill S.; Chapin, F. Stuart, et al., *SCOPE*, **2003**, 61, 15-45.

54. John A. Dean, *Analytical Chemistry Handbook*, McGraw-Hill, **1995**.

55. Chanton J. P., Martens C. S., Biogeochem., **1985**, 1, 375-383.

56. Canfield D. E., Raiswell R., Westrich J. T., Reaves C. M., Berner R. A, *Chem. Geol.*, **1986**, 54, 149-155.

57. Morse J. W., Cornwell J. C., *Mar. Chem.*, **1987**, 22, 55-69.

58. Williamson R. B., Lawrence F. V. D., Wise b. e., Lee D. J., *Intern. J. Environ. Anal. Chem.*, **2001**, 80(3), 187-199.

59. Miguel A. H. D., Richard C., Andre T., *Environ. Sci. Technol.*, **1993**, 27, 2367-2372.

60. Tanmay P., Danielle F., *Water, air, and Soil Pollution*, **2004**, 155, 35-50.

61. Osteryoung, Janet G.; Osteryoung, Robert A. *Anal. Chem.* **1985**, *57*, 101A.

62. Wang, J. *Environ. Sci. Tech.* **1982**, *16*, 104A.

63. Wang, J. *Anal. Chem.* **1982**, *54*, 221.

64. Wiyaratn, W.; Somasundrum, M.; Surareungchai, W. *J. Anal. Chem.* **2004**, 76, 859.

65. Babich, G. A.; Kisil, E. P.; Salikhdzhanova, R. M. F., *J. Anal. Chem.* **1996**, 51, 442.

66. Tushima, M.; Tokuda, K.; Ohsaka, T. *J. Anal. Chem.* **1994**, 66, 4551.

67. Wu, J. F.; Che, Y.; Okajima, T.; Matsumoto, F.; Tokuda, K.; Ohsaka, T. *J. Anal. Chem.* **1999,** 71, 4056.

68. Lee C.; Kwak J.; Bard A. J., *J. Anal. Chem.* **1990**, 62, 1906.

69. Bard, A. J.; Denuault, G.; Friesner, R. A.; Dornblaser, B. C.; Tuckerman, L. S. *Anal. Chem.* **1991**, 63, 1282.

70. Hepel, T.; Osteryoung, J. *J. Phys. Chem.* **1982,** 86, 1406.

71. Kakihana, M.; Ikeuchi, H.; Sato, G. P.; Tokuda, K. *J. Electroanal. Chem.* **1981**, 117, 201.

72. Denuault, G.; Mirkin, M. V.; Bard, A. J. *J. Electroanal. Chem.***1991,** 308, 27.

73. Jung, Y.; Kwak, J. *Bull. Korean Chem. Soc.* **1994**, 15, 209.

74. Bard, A. J.; Faulkner, L. R.; *Electrochemical Methods, Fundamentals and Applications;* John Wiley: New York, **1980**.

75. Christensen, C. R.; Anson, F. C. *J. Anal. Chem.* **1963**, 35, 205.

76. Hubbard, A. T.; Anson, F. C. *Electroanal. Chem.* **1970**, 4, 129.

77. McDuffie, B.; Anderson, L. B.; Reilley, C. N. *Anal. Chem.* **1966**, 38, 883.

78. Konopka, S. J.; McDuffie, B. *Anal. Chem.* **1970,** 42*,* 1746.

79. Sumi, K. *Jpn. Kokai Tokkyo Koho* **2003**, JP 2003050228.

80. Sumi, K. *Jpn. Kokai Tokkyo Koho* **2005**, JP 2005098969.

81. Carslaw, H. S.; Jaeger, J. C.; *Conduction of heat in solids 2nd Ed.*; Oxford, **1959**.

82. John A. Dean. *Analytical chemistry handbook*; McGraw-Hill: New York; **1995**.

83. Wetzel, R.G. *Limnology*, 2nd ed.; Saunders College Pub., **1983**; pp 327.

84. Georg Schwedt. *The Essential Guide to Environmental Chemistry*, translated by Brooks Haderlie; John Wiley and Sons Ltd: New York, **2001**; pp 24.

85. Rozan, Tim F.; Taillefert, Martial; Trouwborst, Robert E. *Limnology and Oceanography*, **2002**, 47, 1346-1354.

86. H. U. Sverdrup; Martin W. Johnson; Richard H. Fleming. *The Oceans*, 12th Printing; Prentice-Hall, Inc: Englewood Cliffs, N. J.; **1978**.

87. Fricke Hugo. *J. Phys. Chem.*, **1953**, 57, 934-937.

88. Guoqing Gu; K. W. Yu. *J. Appl. Phys.*, **1991**, 70, 4476-4479.

89. Hiroyuki Ohshima. *J. Colloid Interface Sci.*, **1999**, 212, 443-448.

90. Constantion Grosse; Kenneth R. Foster. *J. Phys. Chem.*, **1987**, 91, 3073-3076.

91. R. W. O'brien. *J. Colloid Interface Sci.*, **1981**, 81, 234-248.

92. Adrien Cremers; Henty C. Thomas. *J. Phys. Chem.*, **1966**, 70, 3229-3234.

93. Henry C. Thomas; Adrien Cremers. *J. Phys. Chem.*, **1970**, 74, 1072-1075.

94. R. G. Holdich; I. Sinclair. *Powder Technology*, **1992**, 72, 77-87.

95. Fricke Hugo, Phys. Rev., **1925**, 26, 682- 687.

96. Fricke Hugo. *J. General Physiology*, **1924**, 6, 375- 384.

97. Bruggeman, D.A.G. *Ann. Phys.*, **1935**, 24, 636.

98. Looyenga, H. *Physica*, **1965**, 31, 401- 406.

99. F. Bordi, C. Cametti; A. Di Biasio. *J. Phys. Chem.*, **1988**, 92, 4772-4777.

100. Hiroyuki Ohshima. *J. Colloid Interface Sci.*, **2000**, 229, 307-309.

101. Gisèle Bach; Pierre Abelard; Philippe Blanchart. *J. Colloid Interface Sci.*, **2000**, 228, 423-427.

102. Robinson C.D. Cruz; Jörg Reinshagen; Rainer Oberacker; Ana M. Segadães; Michael J. Hoffmann. *J. Colloid Interface Sci.*, **2005**, 286, 579-588.

103. Donald T. Sawyer; Andrzej Sobkowiak; Julian L. Roberts, Jr. *Electrochemistry for Chemists*, 2nd ed.; John Wiley & Sons, Inc.: New York; **1995**.

104. It is noteworthy that, it is possible for parameter *a* to take the value of -1.72 which is the slope of SiO_2 suspension, because SiO_2 is usually the main component of the seabed sludge. However, we will obtain the almost same results as -1.72 is approximate to -1.79.

105. Douglas C. Montgomery; George C. Runger. *Applied Statistics and Probability for Engineers*, 2nd ed.; John Wiley & Sons, Inc.: New York; **1999**; pp 402-404.

106. Fricke Hugo. *Phys. Rev.*, **1924**, 24, 575- 587.

107. Fricke Hugo. *J. General Physiology*, **1924**, 6, 741- 746.

108. M. A. Campo; L. Y. Woo; T. O. Mason; E. J. Garboczi. *J. Electroceramics*, **2002**, 9, 49-56.

109. Hyk W.; Nowicka A.; Stojek Z., *Anal. Chem.*, **2002**, 74, 149-157.

110. Carl H. Hamann, Andrew Hamnett, Wolf Vielstich. *Electrochemistry,* New York, Wiley-VCH, **1998**.

LIST OF PUBLICATION AND PRESENTATION

---------- Publication ----------

L. Yan, N. Takahashi, M. Furue, and K. Sumi, "Rapid Determination of Solid Content in a Suspension and Seabed Sludge by Measurement of Electrical Conductivity," (submitted to *Anal. Chem.*)

K. Sumi, L. Yan, N. Takahashi, Y. Yasuoka "Rapid Determination of Electroactive Species by Chronoamperometry with Twin Electrode and Its Application to the Determination of Iron Sulfide Content in Seabed Sludge," (prepare for submission)

L. Yan, M. Furue, and K. Sumi, "Rapid Determination of Iron Sulfide Content in Sludge of Lake by Electrochemical method with twin electrode," (prepare for submission)

---------- Presentation ----------

Y. Yasuoka, N. Takahashi, L. Yan, M. Furue, and K. Sumi, "Content of Iron(II) Sulfide in the Solid Component of Sludge Determined by Electrochemical Analysis with Twin Electrode," in the 84th Spring Conference of Japanese Chemistry, 1PA-137, Osaka, Japan, March 26~29, 2004.

L. Yan, O.Tsukasa, K. Sumi, M. Furue, "Relationship between Specific Electric Conductivity and Solid Fractional Volume in Suspension with Electrolyte," in the 65th Discussion Conference of Japanese Analytical Chemistry, P2024, Okinawa, Japan, May 15~16, 2004.

Y. Yasuoka, N. Takahashi, L. Yan, K. Sumi, M. Furue, "Content of Iron(II) Sulfide in the Solid Component of Sludge Determined by Electrochemical Analysis with Twin Electrode, " in the 65th Discussion Conference of Japanese Analytical Chemistry, P2082,

Okinawa, Japan, May 15~16, 2004.

L. Yan, Y. Yasuoka, K. Sumi, M. Furue, "Rapid Determination of Fe(II)S Content in the Sludge of Sea and Lake by Electrochemical Techniques, " in the 53th Conference of Japanese Analytical Chemistry, I1018,Chiba, Japan, September 1~3, 2004.

L. Yan, K. Sumi, M. Furue, "Rapid Determination of Iron Sulfide Content in the Sludge of Lake by Electrochemical Methods with twin-electrode" in the 66th Discussion Conference of Japanese Analytical Chemistry, E2013, Hokkaido, Japan, May 14~15, 2005.

L. Yan, K. Sumi, M. Furue, "Rapid Determination of Iron Sulfide Content in the Sludge of Lake by Electrochemical Methods with twin-electrode" in the 54th Conference of Japanese Analytical Chemistry, E3011, Nagoya, Japan, September 14~16, 2005. (**This presentation was awarded "Excellent Oral Presentation Prize".**)

L. Yan, Y. Yasuoka, N. Takahashi, M. Furue, K. Sumi, , "Rapid Determination of Iron Sulfide Content in the Sludge of Bay and Lake by Electrochemical Methods with twin-electrode" in the PACIFICCHEM 2005, Hawaii, USA, December 15~20, 2005.

ACKNOWLEDGEMENT