微量分析およびスペシエーション分析への固相の応用

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Analytical Application of Solid Phase to 
Micro and Speciation Analysis 

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Abstract

Application of the solid phase to the micro and speciation analysis greatly improved the analytical methods including chromatography, i.e., solid phase can be used as the concentration and separation media. For a novel purpose of expanding the application of solid phase to the analytical methodologies, the solid phase could be used as a medium for spectroscopy in solid-phase spectrophotometry (SPS) and as a medium for the chemical reactions in on-line concentration/separation/reaction method by ion exchanger columns. In the present thesis, the two methodologies were used to establish high sensitive, simple, less-cost and greener analytical methods.

In Chapter 1 in Part 1, a new solid-phase spectrophotometry (SPS) method that is easy and simple enough in operation of on-site analyses was developed. A commercially available portable spectrophotometer was optimized for the solid-phase light measurements. LEDs were used as the light source and were powered by rechargeable battery to be usable as portable equipment, and applicability to on-site analyses was realized. The selection of appropriate LED lamps and the stability of the light source were described in detail since they were the important factors for achieving high precision measurements. In addition, the analytical application for the determination of phosphate, chromium(VI) and iron(II) concentrations at µg dm$^{-3}$ levels in natural water samples were conducted to examine the effectiveness of this proposed SPS method.

In Chapter 2 in Part 1, the SPS method was also developed to determine the total iron concentration of boiler water systems in power generation plants. 2,4,6-Tris(2-pyridyl)-1,3,5-triazine method (TPTZ) was used as the coloring reagent for Fe. The reagents and of cation exchanger was put into the boiler water sample, and the produced Fe(TPTZ)$_2$ colored complex was adsorbed on the cation exchanger, resulting a 625 times concentration of the target iron in 30
min without any other procedure. The detection limit of 0.1 µg dm$^{-3}$ was obtained. The optimum conditions for digestion procedure for particulate iron in boiler water and color developing reaction were discussed in detail in this chapter. As for the application to the real samples, the proposed SPS method is the best one because of the shorter analysis time, simpler operation and very low-cost equipment compared to the conventional methods such as TPTZ solution spectrophotometric method, inductively coupled plasma mass spectrometry (ICP-MS) and Atomic absorption spectrometry (AAS).

In Part 2, application of solid phase to the micro and speciation analysis of chemical species was reported. In Chapter 1, speciation analysis of ultratrace chromium in water was realized by on-line reaction/concentration/separation method using a cation exchange column. Cr(VI) and 1,5-diphenylcarbazide (DPC) were mixed and on-line reacted in a flow tube of an HPLC system to form Cr(III)-1,5-diphenylcarbazone (DPCO) complex. When the reagents and complex flowed into the cation-exchange column (TSK IC-Cation, 4.6 mm i.d., 10 mm long), both DPC and the corresponding Cr(III)-DPCO complex were concentrated on the column. The higher DPC concentration on the column accelerated the remaining Cr(VI) to quickly complete the reaction with the DPC on the column. After the complexation and preconcentration, the complex and the extra DPC were eluted with a mixed solution containing lanthanum chloride and 1-propanol. The absorbance of the Cr(III)-DPCO complex at 540 nm was continuously monitored. In addition, the dissolved Cr(III) could be oxidized to Cr(VI) by 185-nm irradiation using a low pressure ultraviolet (UV) lamp for 8 min, and then analyzed by the present method as total chromium, thus the quantitative speciation analysis of Cr(III) and Cr(VI) was realized. The analytical time was 8 min for Cr(VI) and 24 min for total Cr. The detection limit (3σ) of the method was 0.6 ng dm$^{-3}$ for Cr(VI) and 0.8 ng dm$^{-3}$ for total chromium when using a 3.9-cm$^3$ water sample. The
present method was successfully applied to the speciation analysis of dissolved chromium in natural water.

In Chapter 2 Part 2, the application of the method to the speciation analysis of leached Cr(III) and Cr(VI) from stainless steel was reported. Speciation analysis data of leached chromium is very valuable to understand the leaching mechanisms of leaching procedure. Because of the high sensitivity, a small amount of stainless steel sample is enough to obtain a detectable concentration of Cr at interested leaching time. It made the leaching procedure even simpler than the RoHS standard extraction method.

Above all, both the methodologies are very sensitive (detection limit of sub-µg dm\(^{-3}\) level for SPS and ng dm\(^{-3}\) level for the on-line reaction/concentration/separation method) and simple since the pretreatment of the sample can be saved. Especially, the cost of both methods is greatly lower than other sophisticated methods. The SPS methods developed so far can be applied to on-site speciation analysis of unstable chemical species (i.e., Fe(II) in oxic condition) in natural water, and also applicable to the real-time monitoring of special species in industries; the developed on-line reaction/concentration/separation method for speciation analysis of chromium can be applied to various fields in which chromium should be determined, such as the evaluation of environmental pollution potential, regulation of stainless-steel waste management, and the inspection of imported and exported chromium-containing products (i.e., leather, and stainless steel), since a short leaching time is sufficient to obtain a detectable concentration of the chromium because of the high sensitivity.
# CONTENTS

**PREFACE** ......................................................................................................................... 1

**Part 1 ................................................................................................................................. 6**

Chapter 1. Solid-phase spectrophotometer for on-site analysis of trace elements in natural water ............................................................................................................ 6

  Introduction ...................................................................................................................... 6

  Experimental .................................................................................................................. 7

  Results and Discussion ................................................................................................. 10

    Schematic outline of the newly developed system .................................................... 10

    Selection of LEDs ...................................................................................................... 11

    Stability of the light intensity of LED .................................................................... 13

    Procedure to pack the solid beads into the cell ....................................................... 17

    Calibration curves and detection limits ................................................................. 17

  Conclusions .................................................................................................................. 20

  References .................................................................................................................... 21

Chapter 2. Determination of trace iron in the boiler water for power generation plants by solid-phase spectrophotometry ....................................................................................... 22

  Introduction .................................................................................................................. 22

  Experimental ................................................................................................................ 24

  Results and discussion ............................................................................................... 26

    Absorption spectrum of Fe(TPTZ)$_2$ in solid phase .......................................... 26

    Optimum experimental conditions ........................................................................ 27
Interferences of coexisting ions ................................................................. 30

Digestion of the sample ........................................................................... 32

Application of the method ....................................................................... 33

Conclusion ................................................................................................. 35

References .................................................................................................. 36

Part 2 ........................................................................................................... 38

Chapter 1. Speciation analysis of ultratrace chromium in water by on-line
reaction/concentration/separation method using a cation exchange column ............................................. 38

Introduction ............................................................................................... 38

Experimental ............................................................................................. 41

Results and Discussion ............................................................................. 45

Column for the retention of DPC and the complexation .................................. 45

Optimization for Cr(VI) determinations ..................................................... 47

Effects of coexisting ions ......................................................................... 50

Speciation analysis of trace chromium ..................................................... 51

Detection limit, precision and accuracy .................................................... 54

Conclusion ................................................................................................. 57

References .................................................................................................. 58

Chapter 2. Speciation analysis of dissolved chromium leached from stainless steel by on-
line reaction/concentration/separation method .......................................... 61

Introduction ............................................................................................... 61

Experimental ............................................................................................. 62
Results and Discussion ................................................................. 63

Leaching of Cr from SUS304 powder ........................................ 63

Leaching of Cr from SUS631 panel ........................................... 65

Leaching of Cr from SUS304 panel ........................................... 67

Conclusion .................................................................................. 69

References .................................................................................. 70

Conclusion .................................................................................. 71

Acknowledgements ...................................................................... 73
PREFACE

Natural environment is the basis of survival for human beings, from where everything needed for life is supplied. However, as humans developed more and more powerful technologies, demand for various materials has been growing, and human began to extract more resources and energy from the natural environment. Consequently, the environment lost its balance, and many severe environmental problems dramatically began. Inner Mongolia is a typical example of this kind of issues. With the rapid and unreasonable exploitation of resources (mainly coal), there have emerged many severe environmental problems in Inner Mongolia in recent decades. Moreover, the forms of pollution are various, and still the pollution is expanding. The environmental problems in Inner Mongolia attracted many attentions recently. Among them, the pollution of groundwater has a priority since some industries discharge the wastewater into the rivers, streams and/or lakes directly. It is necessary to monitor the natural waters in Inner Mongolia to confirm that the background chemical conditions of natural waters have been maintained, and also to know the early signal of the environmental accidents. For the effective evaluation of natural waters condition, measurement and understanding of the dynamics of trace chemical species in natural waters is essential. However, the concentrations of the chemical species in natural waters are usually very low, and hard to be detected. Therefore, the demand for appropriate, high sensitive, simple, less-cost and greener analytical methods for various species is increasing.

Over decades, many improved analytical methodologies were proposed to cater for the concept of Green Analytical Chemistry in addition to their high analytical effectiveness. Among them, application of the solid phase to the micro and speciation analysis has distinctive features, i.e., solid phase used as the concentration medium for solid phase extraction and as the
separation medium in chromatography. Subsequently, for a novel purpose of expanding the application of solid phase to the analytical methodologies, application of the solid phase as a medium for spectroscopy was proposed as: solid-phase spectrophotometry (SPS), which was first described in 1976.

The point of SPS is that the solid phase is directly measured spectrometrically after the target species is concentrated on it, in other words, the solid phase is used as a concentration media in SPS. Compared to the solid-phase extraction, SPS could skip the procedure of elution of the target analyte from the solid phase. Thus, the dilution of the target solute, and/or other troublesome pretreatment procedure could be avoided. The use of organic solvent as eluent also could be no more necessary, resulting in less consumption of chemicals and less wastes toxic for environment. Some researchers in Europe evaluated that it contributed much to the Green Analytical Chemistry since the consumption of reagents of SPS is usually greatly less than that of the conventional methods. In addition, the volume ratio of the sample solution and the solid beads is very high (for example, 50 cm$^3$ of sample solution and 0.06 cm$^3$ of solid beads), therefore, the sensitivity is higher than that of the conventional solution method by several orders of magnitude. However, SPS has not been widely accepted. One of the reasons may be due to the need to improve the spectrophotometers. A black microcell having a smaller inside volume and 1-cm light-path is suitable for the light measurement of the small amount of solid beads. However, the black microcell causes a large background light attenuation by the cell itself as well as by the solid phase, because the area of the light-path portion of this type of black cell is usually narrower than that of the incident light beam. To overcome these problems, a special compact spectrophotometer applicable to SPS was developed, which consists of a halogen tungsten lamp, a grating and a CCD.
In Chapter 1 in Part 1, the LEDs were used as the light sources instead of conventional halogen tungsten lamp to develop field usable equipment which attain for the purpose of determination of unstable analytes and real-time monitoring of industrial index of certain analytes, since some of the unstable chemical species are very susceptible to the environmental conditions, and a change in the valence state or chemical species may occur in a short time after collecting samples, and in addition, real time monitoring of trace elements has been needed in many industries with low cost. The LED light source could be powered by rechargeable batteries, therefore, the special spectrophotometer could be used for the on-site analysis of real water samples as portable equipment. This improvement was very useful for the on-site determination/real time monitoring of unstable species, such as Fe(II) in natural waters (half-life 1.1 min at pH 8 under oxic conditions). We could determine Cr(VI), Fe(II) and phosphate at field in natural waters by the present SPS system at µg dm$^{-3}$ level or even sub-µg dm$^{-3}$ level.

For the purpose of on-site analysis of unstable species in environmental samples, a portable SPS system was developed in Chapter 1. Then, in order to expand the application of SPS to the industrial samples, a SPS-TPTZ total Fe determination method was developed in Chapter 2. In power generation plants, the total concentration of iron in boiler systems should be monitored in real time as an indicator of corrosion. For that purpose, in Chapter 2 in Part 1, a SPS method for determination of the total iron concentration in boiler water using the special compact spectrophotometer was develop. The iron concentration in the boiler system of power plants was always controlled to be very low (a few µg dm$^{-3}$ level or even sub-µg dm$^{-3}$ level). The TPTZ solution method (JIS B 8224-2005) being used is not sensitive enough, so that long time heating and concentration (16 times) of sample solution is required, which makes operation complicated and troublesome. To save the analytical time, inductively coupled atomic emission spectrometry
(ICP-AES) and ICP-MS are considered to be used for the determination of iron. However, for industries, besides the effectiveness of the determination method, the cost for the machine and maintainance is also a major point. SPS could improve the above problems because of the high sensitivity, simple operation and low cost.

SPS successfully determined the chemical species exist at a few µg dm\(^{-3}\) level or even sub-µg dm\(^{-3}\) level in waters. However, in some case, the concentrations of some special chemical species are even lower than the above level, i.e., ng dm\(^{-3}\) level. Therefore, the application of solid phase was expanded further, application of solid phase as a medium for the chemical reactions: on-line concentration/separation/reaction method by ion exchanger columns, which was first described in 2002 for the determination of boron.

In Part 2 of this thesis, I applied this methodologies and developed a more sensitive method for determination of Cr(VI) of which concentration is even lower than the detection limit of the SPS portable system: ion exchanger (packed in a column) was used as a reaction/concentration/separation media in a flow system. The target species was concentrated on the ion exchanger column to increase the reaction rate, therefore, the reaction time shortened. Then, the target species are eluted for the spectrophotometric detection. The basic idea of this method was first proposed to determine the boron concentration in my lab. In addition, the dissolved Cr(III) could be oxidized to Cr(VI) by 185-nm irradiation using a low pressure ultraviolet (UV) lamp, and then analyzed by the present method as total chromium, thus the quantitative speciation analysis of Cr(III) and Cr(VI) was realized. The detection limit (3σ) under the optimized experimental conditions was 0.6 ng dm\(^{-3}\) for Cr(VI) and 0.8 ng dm\(^{-3}\). River water samples were analyzed by the present method, and the applicability of the developed method to the environmental samples was confirmed in Chapter 1. In order to check the applicability of the proposed method to other
various fields, the speciation analysis of leached Cr from stainless steel was done as an example in Chapter 2 of Part 2. The proposed method is possible to applicable to the rapid speciation analysis of trace Cr leached from various Cr-containing products, such as the items listed in RoHS, because of the high sensitivity and high reproducibility.

Both the methodologies indeed expanded the application of solid phase for the micro and speciation analysis, and both are very sensitive (detection limit of sub-µg dm$^{-3}$ level for the former and ng dm$^{-3}$ level for the latter) and simple since the pretreatment of the sample can be saved. Especially, the cost of both methods is greatly lower than other sophisticated methods.
Part 1

Chapter 1. Solid-phase spectrophotometer for on-site analysis of trace elements in natural water

Introduction

Some of the unstable chemical species are very susceptible to the environmental conditions, and a change in the valence state or chemical species may occur in a short time after collecting samples. In addition, real time monitoring of trace elements concentration has been needed in many industries with low cost. Therefore, the development of on-site analysis method is very important.

In solid-phase spectrometry (SPS),\(^1\)\(^,\)\(^2\) because the analyte is spectrometrically determined without desorption from the solid phase, the dilution of the analyte does not occur and therefore a higher sensitivity can be obtained. SPS is very useful for the determination of trace chemical components present at µg dm\(^{-3}\) levels in water, however, SPS has not been widely accepted. One of the reasons may be further improvement of the spectrophotometers. The use of a smaller volume of the solid phase effectively enhances the sensitivity of the SPS,\(^3\) and black microcells having a smaller inside volume and 1 cm light-path are suitable for my purpose.\(^3\)\(^,\)\(^4\) On the other hand, the use of this type black microcell has disadvantages that a large background light attenuation by the cell itself as well as by the solid phase occur, because the area of the light-path portion of this type of black cell is usually narrower than that of the incident light beam\(^5\).

In order to overcome these problems, a novel modification of SPS, which is easy and simple in operation enough to be applicable to on-site analyses, was proposed in this study. A commercially available portable spectrophotometer was optimized for solid-phase light
measurements. The main characteristics of this improved SPS method as well as the analytical application for the determination of phosphate, chromium (VI) and iron (II) at µg dm$^{-3}$ levels in natural water samples were carried out.

**Experimental**

*Reagents and chemicals*

All reagents were of analytical grade. Highly purified water was prepared by a Milli-Q Advantage A10 system (Millipore, Molsheim, France).

The standard phosphate solution (1000 mg dm$^{-3}$) was obtained from Wako, Osaka, Japan. A combined reagent solution to form molybdenum blue species was prepared as described in a previous paper: mixing 20 cm$^3$ of 2.5 mol dm$^{-3}$ sulfuric acid (70 cm$^3$ of concentrated sulfuric acid diluted to 500 cm$^3$ with water), 2 cm$^3$ of a potassium antimonyl tartrate solution (0.274 g of potassium antimonyl tartrate hemihydrate dissolved in 100 cm$^3$ of water), 6 cm$^3$ of a 4 % (w/v) ammonium molybdate solution, and 12 cm$^3$ of a 0.1 mol dm$^{-3}$ ascorbic acid solution (1.76 g of ascorbic acid in 100 cm$^3$ of water). The Sephadex G-25 gel (Medium) was purchased from GE Healthcare Bio-Sciences, Uppsala, Sweden.

The standard chromium (VI) solution (1000 mg dm$^{-3}$) for AAS was obtained from Kishida, Osaka, Japan. All reagent solution for color development of chromium (VI) was prepared as described in a previous paper, dissolving 0.25 g DPC (dophenylcarbazide, Wako, Osaka, Japan) in 100 cm$^3$ of acetone. The Muromac 50W-X2 cation exchanger (100-200 mesh) was purchased from Muromachi, Tokyo, Japan.

The standard iron (II) stock solution (1000 mg dm$^{-3}$) was prepared by dissolving 0.498 g FeSO$_4$·7H$_2$O in 11.0g of 36% HCl solution and diluted to 100 cm$^3$ with water. The combined
solution of chromogenic reagent and buffer solution for iron (II) was prepared by dissolving 0.2 g of 1,10-phenanthroline and 7.7 g of ammonium acetate in 5.74 cm$^3$ of 99.7% acetic acid and diluted to 100 cm$^3$. A 1 mol dm$^{-3}$ hydrochloric acid was prepared by diluting 8.6 cm$^3$ of 36% HCl to 100 cm$^3$ with water. A 1 mol dm$^{-3}$ ammonia solution was prepared by diluting 6.8 cm$^3$ of 28% ammonia solution to 100 cm$^3$ with water.

Devices and equipment

The daylight color LED (LP-H508H238WC, 24-31 cd) and pink color LED (LP-5034FWC-WR, 5-8 cd) were commercially available from the Peace Corp., Koshigaya, Japan. A black cell (Fig. 1) having a light-path length of 10 mm and a 2-mm width (M20-B-2, GL Sciences, Tokyo, Japan) was developed for the absorbance measurement of small amount of solid phase. Battery-driven magnetic stirrers were used for on-site analysis. A constant volume of the gel was taken using aliquotting device: a PTFE tube (1.0-mm i.d. and 7-cm length) was fitted on the side with a PP resin filter tip and connected to a 10-cm$^3$ disposable syringe.$^{3,4}$

A portable single beam type spectrophotometer (Fig. 2) for the SPS, Model SP-101 (W250 × D100 × H50 mm), was commercially available from Satoda Science, Hiroshima, Japan. It contained a halogen tungsten lamp or LED as the light source, a grating (600 lines/mm) as the monochromator, a CCD array (2048 bit) as the light detector (measurable wavelength: 400-850 nm, resolution: 2.5 nm), and a laptop PC as the data processor. In this study, LEDs were used as the light source. A 1.2 mm thick PTFE film, which showed a constant light scattering behavior similar to that of solid beads packed in the cell, was used as a reference.
Procedures for the determination of phosphate, chromium(VI) and iron(II)

All of the water samples were filtered through a 0.20-µm PTFE membrane filter (Advantec, Tokyo) at the site where the samples were collected.

**Phosphate.** First, 3.2 cm$^3$ of the combined reagent and 0.06 cm$^3$ of the gel beads were added to a 20-cm$^3$ water sample containing 1-10 µg dm$^{-3}$ of phosphate-P in a polyethylene bottle. The contents were mixed for 30 min to concentrate the target analyte into the gel phase as the colored species. After a short time to allow the resin beads to settle to the bottom of the reaction container, the supernatant solution was removed, and an approximate 1-cm$^3$ volume of the gel beads and reaction solution mixture was transferred into the cell (Fig. 1) using a pipette. The light intensity at 640 nm (strong-absorption wavelength, $\lambda_1$), $I_{R(\lambda_1)}$, and that at 450 nm (weak-absorption wavelength, $\lambda_2$), $I_{R(\lambda_2)}$, of the PTFE film were first measured as the reference, and the sample cell was then inserted in the cell holder to record the light intensities at the two wavelengths, $I_{(\lambda_1)}$ and $I_{(\lambda_2)}$. In Eq (1), $\Delta A$ corresponds to the amounts of the blue complex between phosphate and molybdate, and this equation was used for the determination of phosphate.

$$\Delta A = \log \left( \frac{I_{R(\lambda_1)}}{I_{(\lambda_1)}} \right) - \log \left( \frac{I_{R(\lambda_2)}}{I_{(\lambda_2)}} \right)$$

(1)

After the measurement, the solid beads were removed from the cell for the next measurement.

**Chromium(VI).** To a 20 cm$^3$ water sample containing 1.0 cm$^3$ of a 2000 mg dm$^{-3}$ Ca$^{2+}$ solution, 1.0 cm$^3$ of a 0.5 mol dm$^{-3}$ H$_2$SO$_4$ solution and 0.5 cm$^3$ of a coloring agent solution, 0.06 cm$^3$ of the ion exchanger was added, then the mixture was stirred for 30 min at 25°C. After transferring the resin beads to the cell in the same way as described for the determination of phosphate, the light attenuances at $\lambda_1 = 540$ nm and $\lambda_2 = 680$ nm were measured and $\Delta A$ was used for the determination of chromium(VI).
Iron(II). Natural water samples were collected through a PTFE tube (3 mm i.d.) using a plastic syringe (50 cm$^3$) attached to a three-way stopcock under a nitrogen atmosphere, filtered through 0.20-μm PTFE membrane filters (Advantec) and immediately acidified to pH 2 with HCl under a nitrogen atmosphere.

To a 25 cm$^3$ sample, 0.5 cm$^3$ of the mixed coloring reagent and buffer solution, 0.25 cm$^3$ of a 1 mol dm$^{-3}$ NH$_3$ solution and 0.06 cm$^3$ of Muromac 50W-X2 resin were added. After a 30-min stirring, the solid beads were transferred into the microblack cell and light attenuances at $\lambda_1 = 512$ nm and $\lambda_2 = 650$ nm were measured. Then, $\Delta A$ was used for the determination of iron(II).

Results and Discussion

Schematic outline of the newly developed system

For the absorbance measurement of the solid phase, it is fairly difficult to maintain the same packing condition for every sample, which affects the attenuation at the absorption maximum wavelength. To minimize the error caused by the packing state difference of the solid beads in the cell for each measurement, the absorbances of the solid phase were measured at the maximum-absorption wavelength ($\lambda_1$ nm) and weak or no-absorption wavelength ($\lambda_2$ nm), and then the difference in the attenuances ($\Delta A = A(\lambda_1 \text{ nm}) - A(\lambda_2 \text{ nm})$) was used for the quantitative analysis of the target analyte.$^{1,2}$ The portable spectrophotometer is shown in Fig. 2. The CCD array together with the gratings made it possible to continuously and simultaneously monitor the $\Delta A$.

A black cell (Fig. 1) having a light-path length of 10 mm and a 2-mm width (M20-B-2, GL Sciences, Tokyo, Japan) was developed to pack the small volume of solid particles on which the target color species was concentrated. A part of a 5-cm$^3$ polypropylene tip was attached to the
cell for easier introduction of the solid slurry. If the light intensity of the LED was weak, a ball lens (1-cm diameter) between the light source and the cell was effective to collect the incident light beam at the entrance of the light path portion of the cell (Fig. 2). A Ni-Cd battery (12 V) was used to power the LED.

Selection of LEDs

The light intensity profiles of the LEDs and halogen tungsten lamp are shown in Fig. 3. The strong light intensity wavelengths of the LEDs were different from one another, and narrower than the wavelength range of the halogen tungsten lamp. Therefore, the LEDs should be selected according to the absorption wavelength of the target complexes. The daylight LED with a stronger light intensity in the longer wavelength region was better than the white LED for the determination of chromium (VI) and iron (II), because the light intensity at $\lambda_2 = 680$ nm or $650$ nm had to be also measured. The pink LED, which has a strong light intensity around 450 nm and 640 nm, was used for the determination of phosphate.

Fig. 1. Black microcell. A: polypropylene tip; B: Black microcell (light-path length: 10 mm; width: 2 mm). The parts A, and B were fixed by an epoxy resin adhesive. For practical use, the cell was masked by black paint to make a window of 1 mm height at the bottom of the cell.
Fig. 2. Simple spectrophotometer for SPS. Light source: LED.

Fig. 3. Light intensity profiles. A: pink LED, B: white LED, C: daylight LED, D: halogen tungsten lamp.

Solid phase: Sephadex G-25; Cell length: 10 mm.
Stability of the light intensity of LED

The spectrophotometer used was a single beam type, and therefore, the stability of the light intensity was critical for high precision measurements. For the tungsten halogen lamp, the light intensities in the visible region were stable enough to allow a quantitative spectrophotometric determination. However, for the LEDs, the light intensity might change with the time and temperature.\(^6\,^7\)

To examine the time and temperature dependence of LED light intensity, a series of experiment were done.

First, the light intensity that has passed through a 0.06 cm\(^3\) Muramac 50W-X2 cation exchanger (100-200 mesh) was measured under the condition of continuing to turn on the LED light for 4 hrs at stable temperature. At a constant temperature, the light intensities fairly decreased in the beginning just after turning on the light, and almost became constant after 20 min as shown in line 1 and 2 in Fig. 4. We determined that the light measurements should be started then. Using the PTFE film, the absorbance was obtained, and line 1 in Fig. 5 shows the time dependence of the difference of the absorbances of the two wavelengths (\(\Delta A\)), which was used for the quantitative analysis of target elements, showing that \(\Delta A\) was fairly constant through out the experimental time under the condition of continuing to turn on the LED light and stable temperature. The stable light intensity could continue at least 12 h according to experimental data.

Then, the next experiment was done. The same resin beads and the same LED were used. After 2 hr measurement of the light intensity at 22°C, the temperature was increased to 30 °C under the condition of continuing to turn on the LED light, and the light intensity was measured for another 2 hrs. Line 3 and 4 in Fig. 4 show the temperature dependence of the LED light

13
intensity. The light intensities fairly decreased when the temperature increased. In Fig. 5, line 2, a large decrease in the $\Delta A$ could be observed.

For the trace analysis, even if a slight change in the absorbance may cause a big error in the concentration. Therefore, the third experiment was done to overcome the fluctuation of light intensity caused by the temperature change. The absorbance of the reference and the target solid phase were alternatively measured, it means, the reference was measured just before every sample measurement. The temperature was increased in the same way mentioned in experiment 2. The light intensities of a PTFE film were measured instead of a sample beads layer because the solid beads layer was not so stable due to air bubbles generated for a long period experiment. Fig. 6 shows the result. Although the $\Delta A$ (Fig. 6 (B)) was not as constant as shown in the experiment 1, but, in this way, the big fluctuation caused by the temperature change could be reduced even if the light intensities changed (Fig. 6 (A)) during the measurement.

For on-site analysis, it is hard to control the environmental temperature. Therefore, the reference measurement just before every sample measurement is effective to reduce the errors caused by the light intensity fluctuation.
Fig. 4 Time and temperature dependence of light intensity. LED: daylight type; Solid phase: Muramac 50W-X2 cation exchanger (100-200 mesh); Line 1 and 2: constant temperature, 25 °C. Line 3 and 4: 0-120 min, 22 °C; 120-240 min, 30 °C.

Fig. 5 Time dependence effect of absorbance. LED: daylight type; Solid phase: Muramac 50W-X2 cation exchanger (100-200 mesh); Line 1: constant temperature, 25 °C. Line 2: 0-120 min, 22 °C; 120-240 min, 30 °C.
Fig. 6 Temperature dependence of light intensity and absorbance of LED. (A): light intensity; a: 650 nm, b: 520 nm; (B): ΔA. LED: daylight; Solid phase: 1.2 mm PTFE film; Temperature: 0-60 min, 21 °C; 60-120 min, 31 °C. For ΔA, the reference measurements were taken just before every sample measurement.
Procedure to pack the solid beads into the cell

As already mentioned, the smaller the volume of the solid beads, the higher the sensitivity. The minimum amount of resin necessary for complete packing in the black cell was examined and found to be 0.06 cm$^3$. This small volume of the resin could be taken and transferred to a water sample using a resin aliquotting device. After the adsorption of the colored species, the mixture was stored for a short moment to settle the solid beads, and then the solid beads were transferred to the cell (Fig. 1) with a small amount of solution using a pipette.

Calibration curves and detection limits

Phosphate. The performances of this new instrument and the cell were examined using the SPS phosphate determination method, which has already been well established. When using the pink LED as the light source, sensitivity was somewhat lower than that of when the halogen tungsten lamp was used, because the molar absorptivity of the molybdenum blue species at 640 nm was lower than that at 700 nm (the calibration curve: $\Delta A = 0.0278 P$ (µg dm$^{-3}$) – 0.192 ($R^2 = 0.990$)). The detection limit corresponding to the 3σ of the blank test $\Delta A$ was 0.3 µg P dm$^{-3}$. A natural water sample collected from the Nanatsugama limestone cave, Saikai, Nagasaki was analyzed. The dissolved phosphate concentration was $2.3 \pm 0.1$ µg dm$^{-3} (n = 3)$ and the relative standard deviation was around 5%. The results of the recovery test of the same water sample are shown in Table 1, and almost all of the added phosphate was recovered.

Chromium(VI). The daylight LED was used as the light source for the chromium(VI) determination, and the calibration curve could be expressed as $\Delta A = 0.0676 Cr$ (µg dm$^{-3}$) + 0.060 ($R^2 = 0.992$). The detection limit was 0.6 µg Cr dm$^{-3}$. A well water sample from the Hakozaki...
The dissolved chromium(VI) concentration was 4.3 ± 0.2 µg dm$^{-3}$ (n=4). The results of the recovery test of chromium(VI) are shown in Table 2, and ± 10% error may be included in the results of the on-site analysis.

Iron(II). For the iron(II), 1,10-phenanthroline was used as the coloring reagent. The same daylight LED was used as the light source. The calibration curve was $\Delta A = 0.053$ Fe (µg dm$^{-3}$) – 0.039 ($R^2 = 0.992$). The detection limit was 0.3 µg Fe dm$^{-3}$. A water sample collected from a small unpolluted stream from Kawachi, Fukuoka, was quantitatively analyzed, and the dissolved Fe(II) concentration was 3.0 ± 0.1 µg dm$^{-3}$ (n=4), suggesting that the Fe(II) may be supplied from the bottom of the stream under local anoxic conditions. The results of the recovery test of Fe(II) are shown in Table 3. In a previous study using the spectrophotometer with an LED light source, the results of the recovery tests of Fe(II) (1,10-phenanthroline method) were shown, and the recovery ranged from 93% to 105% at mg dm$^{-3}$ levels. Our results are acceptable for the on-site analysis of Fe(II) at µg dm$^{-3}$ levels.
Table 1 Recovery test by the standard-addition method using natural water sample

<table>
<thead>
<tr>
<th>P added / µg dm$^{-3}$</th>
<th>P found / µg dm$^{-3}$</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.29 ± 0.11</td>
<td>(100)</td>
</tr>
<tr>
<td>1.99</td>
<td>4.24</td>
<td>99</td>
</tr>
<tr>
<td>2.03</td>
<td>4.28</td>
<td>100</td>
</tr>
<tr>
<td>3.00</td>
<td>5.36</td>
<td>101</td>
</tr>
<tr>
<td>3.03</td>
<td>5.32</td>
<td>101</td>
</tr>
<tr>
<td>4.00</td>
<td>6.76</td>
<td>107</td>
</tr>
<tr>
<td>4.01</td>
<td>6.80</td>
<td>108</td>
</tr>
</tbody>
</table>

Light source: pink LED
Sample: Groundwater emerging from Nanatsugama limestone cave.

Table 2 Recovery test by the standard-addition method using well water sample

<table>
<thead>
<tr>
<th>Cr(VI) added / µg dm$^{-3}$</th>
<th>Cr(VI) found / µg dm$^{-3}$</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.33 ± 0.15</td>
<td>(100)</td>
</tr>
<tr>
<td>1.01$^b$</td>
<td>3.29</td>
<td>112</td>
</tr>
<tr>
<td>1.07$^b$</td>
<td>3.29</td>
<td>106</td>
</tr>
<tr>
<td>2.00$^b$</td>
<td>4.34</td>
<td>109</td>
</tr>
<tr>
<td>1.98$^b$</td>
<td>4.31</td>
<td>108</td>
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<tr>
<td>2.96$^b$</td>
<td>4.82</td>
<td>90</td>
</tr>
<tr>
<td>3.04$^b$</td>
<td>4.92</td>
<td>91</td>
</tr>
</tbody>
</table>

Light source: daylight LED
Sample: Well water sample from Hakozaki campus, Kyushu University, Fukuoka; $^b$The sample solution was diluted twice with water.

Table 3 Recovery test by the standard-addition method using natural water sample

<table>
<thead>
<tr>
<th>Fe(II) added / µg dm$^{-3}$</th>
<th>Fe(II) found / µg dm$^{-3}$</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.97 ± 0.08</td>
<td>(100)</td>
</tr>
<tr>
<td>0.93</td>
<td>3.96</td>
<td>107</td>
</tr>
<tr>
<td>3.83</td>
<td>93</td>
<td></td>
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<tr>
<td>3.93</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>4.55</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>4.70</td>
<td>93</td>
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<tr>
<td>4.63</td>
<td>89</td>
<td></td>
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<td>5.21</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>5.29</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>5.42</td>
<td>88</td>
<td></td>
</tr>
</tbody>
</table>

Light source: daylight LED
Sample: Small stream water sample from Kawachi, Fukuoka.
Conclusions

The use of LED as a light source for the simple portable spectrophotometer allows us to use a battery as the power source for our equipment, and therefore on-site analyses can be realized. Although the light intensity of the LEDs changed with the temperature, the errors could be suppressed by the measurement of the reference just before every sample measurement.

This system also made it possible to reduce the consumption of reagents and waste generation. It made the analytical methods more environmentally friendly, and therefore, the SPS significantly contributed to Green Analytical Chemistry. Many spectrophotometric methods for various trace elements and/or substances present at µg dm⁻³ levels in water, especially of unstable species, such as Fe(II) under oxic conditions, can be applied to on-site analyses using our method and equipment. At present, over 10% errors may be included in the analytical results when using the LED as the light source for the µg dm⁻³ level analyte. However, further study on LEDs and light measurements of the solid beads layer should improve the reproducibility of the measurements.
References


Chapter 2. Determination of trace iron in the boiler water for power generation plants by solid-phase spectrophotometry

Introduction

Corrosion has a major concern on the efficiency and reliability of electric power plants.\(^1\) Tube corrosion is known to be the main cause of the boiler failure, and at its worst, a single corrosion failure makes a plant inoperable.\(^{1,2}\) The total cost of boiler tube failures in power plants is estimated to be about 5 billion dollars a year,\(^3\) and accidents interrupt the power supplies to tens of thousands of consumers temporarily. Scale deposits in boiler system are another main concern since they considerably decrease the efficiency of energy.\(^2\) For thermal power plants, the economic losses caused by the boiler failure has a priority. However, in the nuclear power plants, the safety risk of release of dangerous chemicals into environment has a higher priority. Various chemical and physical treatments are taken to the boiler water system to control the corrosion processes.\(^{4-6}\) As the indicator of the scale and corrosion occurrence in the boiler, it has been regulated according to the Japan Industry Standard that iron concentration should be controlled lower than 10 \(\mu\)g dm\(^{-3}\) for all-volatile treatment system and lower than 5 \(\mu\)g dm\(^{-3}\) for oxygenated treatment system.\(^7\) For the purpose of monitoring such a low concentration of iron, a sensitive detection method of which detection limit reaches sub-ppb level is needed. The TPTZ solution method (JIS B 8224-2005) is not sensitive enough, so that the 16 times concentration of sample solution by long time heating is required, which makes the operation complicated and troublesome. To save the analytical time, ICP-AES and ICP-MS are considered to be used for the determination of iron. However, besides the effectiveness of the determination method, the cost for the machine and maintenance is also a major point for industries.
Solid phase spectrometry (SPS) can improve the above problems because of the high sensitivity, simple operation and low cost. SPS means a direct absorption measurement of solid beads on which the colored analyte was adsorbed. In the sense of concentration, the efficiency of SPS is significantly greater than that of evaporation concentration. For example, in the solution spectrometric method, an 800 cm$^3$ boiler water sample has to been evaporated/concentrated to 50 cm$^3$ by heating for 4 - 5 h to obtain a measurable concentration of iron. However, in present SPS method for iron determination, 0.08 cm$^3$ cation exchanger is added into 50 cm$^3$ boiler water sample, and mixed for 30 min to adsorb/concentrate the colored analyte on the solid beads, resulting a 625 times concentration of the target analyte in 30 min without any other procedure. Therefore, the sensitivity of SPS is several orders of magnitude greater than the solution method, and the procedure is much simpler. In addition, the 30 min-mixing can be done in a closed container to avoid the iron contamination in the experimental environment.

In this study, 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) was used as the coloring reagent. TPTZ was reported to form a intense violet color 2:1 complex (Fe(TPTZ)$_2^{2+}$) with Fe(II), and used for the determination of total iron in various samples. The complex has an absorption maximum at 593 nm, and at least stable for 32 h in aqueous solution. The molar absorptivity of the complex is known to vary slightly in different solvents, and $2.26 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$ in water. TPTZ method has the advantage to be free from common interferences. The present SPS method greatly improved the sensitivity of the TPTZ coloring method for total iron determination, and made it possible to detect the sub-$\mu$g dm$^{-3}$ level total iron in water samples without any special expensive equipment.
**Experimental**

**Reagents**

Highly purified water prepared with a Milli-Q SP system (Millipore, USA) was used throughout the study. A standard Fe(III) solution (500 µg dm$^{-3}$) was prepared by diluting a 1000 mg dm$^{-3}$ atomic absorption standard solution (Wako, Osaka) with water and acidified to pH 2 with hydrochloric acid. Hydrochloric acid (1+1) was prepared by diluting 36% hydrochloric acid (for trace analysis, Wako) with water. The buffer solution (6 mol dm$^{-3}$) was made by mixing ammonia solution (ultrapure, 28.0%, Kanto), formic acid (for trace analysis, 98.0%, Kanto), and highly purified water by the volume ratio of 2:1:2. A coloring reagent 2,4,6-Tris(2-pyridy)-1,3,5-triazine (TPTZ) solution was prepared by dissolving 0.32 g TPTZ (Wako, Tokyo) into 1 cm$^3$ (1+1) hydrochloric acid, and then diluted to 500 cm$^3$ with water. A reducing agent (hydroxylammonium chloride) solution (10%) was made by dissolving 10 g of hydroxylammonium chloride (Wako) into water and made up to 100 cm$^3$. The Muromac 50W-X2 cation exchanger (100 - 200 mesh) was purchased from Muromachi, Tokyo, Japan.
**Devices and equipment**

The equipments used for the light measurement were just as described in Chapter 1.\(^{14}\) However, the light source used in this Chapter was the conventional halogen tungsten lamp, as shown in Fig. 2. A convex lens (focal distant 20 mm, Sugitoh, Tokyo, Japan) was placed between the incident light window and the cell for weakly focusing the light beam at the light-beam entrance of the cell. The sample cell used was as shown in Fig. 1 of Chapter 1.\(^{15}\) A constant volume of the resin beads was taken using an aliquotting device: A PTFE tube (1.0-mm i.d. and 7-cm long) was fitted on the side with a PP resin filter tip and connected to a 10-cm\(^3\) disposable syringe.\(^{16,17}\)

A heating bath (ADVANTEC) was used for preparing boiling water for the sample digestion procedure.

![Fig. 2 Compact spectrophotometer](image)

**Analytical procedure for measurement by solid-phase spectrophotometry**

To a 50-cm\(^3\) boiler water sample 2.5 cm\(^3\) of (1+1) hydrochloric acid was added, and then the solution was allowed to stand in boiling water to digest particulate matter containing iron for at least 30 min. Then, the water sample was allowed to cool down to the room temperature, and 1 cm\(^3\) of the hydroxylammonium chloride solution, 2 cm\(^3\) of TPTZ solution, 3.5 cm\(^3\) of formic acid-ammonia buffer solution, and 0.08 cm\(^3\) of Muromac 50W-X2 resin were added in a regular order. Next, the mixture was stirred for 30 min at 25°C in the thermostat bath. The colored resin
beads were collected and packed into the black microcell (light path length 10 mm, 2 mm width) with a pipette. The absorbances at 610 nm (absorption maximum wavelength) and 750 nm (weak-absorption wavelength) were measured using the single-beam type spectrophotometer. The difference of the absorbances at two wavelengths (ΔA) was used for iron determination.

**Results and discussion**

*Absorption spectrum of Fe(TPTZ)$_2$ in solid phase*

The water solution of the produced complex of Fe(II) and TPTZ reaction was reported to show absorption maximum at wavelength 593 nm in many previous papers. However, in this study, the existing media of the complex was a cation exchanger resin (50W-X2, 100-200 mesh), therefore the absorption maximum was moved to wavelength 610 nm. The absorption spectrum was shown in Fig. 3. For the absorbance measurement of the solid phase, it is fairly difficult to maintain the same packing condition for all samples, which affects the attenuance at the absorption maximum wavelength. To minimize the error caused by the packing state difference of the solid beads in the cell for each measurement, the absorbances of the solid phase were measured at the maximum-absorption wavelength ($\lambda_1$ nm) and weak or no-absorption wavelength ($\lambda_2$ nm), and then the difference in the attenuances ($\Delta A = A(\lambda_1 \text{ nm}) - A(\lambda_2 \text{ nm})$) was used for the quantitative analysis of the target analyte. Therefore, light attenuances at wavelengths 610 nm (maximum-absorption wavelength) and 750 nm (weak absorption wavelength) were chose to measured, then, ΔA was used for the determination of total iron.
Fig. 3 Absorption spectrum of Fe(TPTZ)$_2$ complex in solid phase

Fe concentration: 5 µg dm$^{-3}$; Solid phase: 0.08 cm$^3$ of Muromac 50W-X2 cation exchanger (100 - 200 mesh).

**Optimum experimental conditions**

*Effect of pH on the color development.* It was reported that the Fe(TPTZ)$_2^{2+}$ complex was stable in the pH range 3.4-5.8. However, later some researchers confirmed that both H$^+$ and OH$^-$ accelerate the dissociation of Fe(TPTZ)$_2^{2+}$ complex. Therefore, the developed color fades quickly in strong acidic solution pH lower than 3; In addition, the precipitation caused by the hydrolysis of Fe(III) in weak acidic solution (pH higher than 3.8) was also reported, which was also a reason to hinder the formation of Fe(TPTZ)$_2^{2+}$ complex. The result of pH effect on color development of this study was shown in Fig. 4, indicating that the range of pH 3 - 4 was best for the formation of Fe(TPTZ)$_2^{2+}$ complex.
Fig. 4 pH dependence of absorbance at 610 nm

Sample solution: 50 cm$^3$; Fe: 5 µg dm$^{-3}$; Solid phase: 0.08 cm$^3$ of Muromac 50W-X2 cation exchanger (100 - 200 mesh).

*Effect of stirring time on the absorbance.* The effect of the stirring time on the absorbance at 610 nm was investigated and the result was shown in Fig. 5. The absorbance increased with the increasing stirring time in the experimental time period (20 - 40min). Because of the reason for saving time, stirring time was fixed at 30 min in this study.

Fig. 5 Time dependence of absorbance at 610 nm
Sample solution: 50 cm$^3$; Fe: 3 µg dm$^{-3}$; Solid phase: 0.08 cm$^3$ of Muromac 50W-X2 cation exchanger (100 - 200 mesh).

**Effect of temperature on the color development.** The effect of experimental temperature on absorbance was examined by varying the temperature from 15 to 40 °C using the thermostated bath. The results showed that the absorbance was temperature-dependent as shown in Fig. 6. The absorbance increased with the increase in the temperature and the effect was especially significant when the temperature was below 20°C. Therefore, to improve reproducibility of the method, it is necessary to keep the experimental temperature constant. For reasons of practical analytical measurements, the room temperature (25°C) was chosen in the experiment.

![Fig. 6 Temperature dependence of absorbance at 610 nm](image)

Sample solution: 50 cm$^3$; Fe: 3 µg dm$^{-3}$; Solid phase: 0.08 cm$^3$ of Muromac 50W-X2 cation exchanger (100 - 200 mesh).

**Effect of TPTZ concentration on the color development.** The influence of TPTZ concentration on determination was examined in the range from 0.02 mmol dm$^{-3}$ to 0.14 mmol dm$^{-3}$ as shown in Fig. 7. A very slight change was observed in the experimental concentration range of TPTZ since
even the lowest one (0.02 mmol dm\(^{-3}\)) was much higher than the determined iron concentration (3 µg dm\(^{-3}\) = 5.4 × 10\(^{-5}\) mmol dm\(^{-3}\)). To force the reaction to completion, the TPTZ concentration was fixed at 0.08 mmol dm\(^{-3}\).

![Graph](image)

**Fig. 7 Effect of TPTZ concentration on complexation**

Sample solution: 50 cm\(^3\); Fe: 3 µg dm\(^{-3}\); Solid phase: 0.08 cm\(^3\) of Muromac 50W-X2 cation exchanger (100 - 200 mesh).

**Interferences of coexisting ions**

The water used for the boiler systems in power plants is always deionized previously, therefore, the concentrations of various ions are fairly low in the feed water. However, to evaluate the applicability of the TPTZ-SPS method, interferences from coexisting ions were examined, and the results were shown in Table 1. Mn\(^{2+}\), Cr\(^{3+}\), and Cd\(^{2+}\) gave no interferences at the existing level of 1 mg dm\(^{-3}\) when the determined Fe concentration was 2.5 µg dm\(^{-3}\). Compared to these ions, the interferences of Ni\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\), and MoO\(_4^{2-}\) were slightly more significant, 1 mg dm\(^{-3}\) of these ions resulted in several tens of percent of errors for the
determination of 2.5 µg dm$^{-3}$ of total iron. However, 200 µg dm$^{-3}$ of these ions resulted in tolerable errors (about ±5%). The interference of Co$^{2+}$ was most significant among the tested ions; the concentration low enough to 2.5 µg dm$^{-3}$ reluctantly resulted in a tolerable error. However, the concentrations of Co$^{2+}$ and the other tested ions in the boiler water systems were not high enough to cause such significant errors, therefore, the concern about the interferences can be saved for the SPS-TPTZ total iron determination method.

Table 1 Interferences of coexisting ions for total iron determination by SPS method

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration / µg dm$^{-3}$</th>
<th>Added Fe / µg dm$^{-3}$</th>
<th>Found Fe / µg dm$^{-3}$</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{2+}$</td>
<td>1000</td>
<td>2.52</td>
<td>2.64</td>
<td>+4.8</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>1000</td>
<td>2.50</td>
<td>1.33</td>
<td>-46.7</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>2.51</td>
<td>2.62</td>
<td>+4.5</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>1000</td>
<td>2.51</td>
<td>2.62</td>
<td>+4.4</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>1000</td>
<td>2.50</td>
<td>1.69</td>
<td>-32.5</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>2.50</td>
<td>2.36</td>
<td>-5.5</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>1000</td>
<td>2.54</td>
<td>1.81</td>
<td>-28.8</td>
</tr>
<tr>
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<td>200</td>
<td>2.52</td>
<td>2.39</td>
<td>-5.2</td>
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<tr>
<td>Cd$^{2+}$</td>
<td>1000</td>
<td>2.54</td>
<td>2.58</td>
<td>+1.5</td>
</tr>
<tr>
<td>MoO$_4^{2-}$</td>
<td>1000</td>
<td>2.49</td>
<td>2.89</td>
<td>+16.0</td>
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<td>+15.6</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.53</td>
<td>2.67</td>
<td>+5.6</td>
</tr>
</tbody>
</table>
**Digestion of the sample**

For the purpose of inhibiting the acid attack corrosion of a boiler system, pH of the feed water is generally adjusted to 8-9 (even pH 11) in power plants. Under the weak alkaline condition, iron is easy to form hydroxides and/or oxides, and exists as colloid and precipitation. This study needs to determine the total concentration of iron including ionic state, colloidal and particulate iron in the boiler system. Therefore, the colloidal and particulate iron in the boiler water should be dissolved to ionic iron before the quantitative analysis of total amount of iron in the water.

To obtain a complete digestion of the colloidal and precipitated iron in the sample, an effective digestion way was needed. Heating the sample solution with strong acid in boiling water was chosen as the digestion way in this study. In Fig. 8, the time dependence of the digestion in boiling water was shown, and the results of two samples indicated that 30 min was enough to digest the colloidal and particulate form of iron in the sample.

![Fig. 8 Time dependence of digestion of colloidal and particulate Fe](image_url)
Application of the method

An example of the calibration curve plotted between the absorbance of the complex versus the Fe concentration was shown in Fig. 9, with a slope of 0.285 and a correlation coefficient of 0.997. For the total iron determination, the detection limit was defined as the concentration that gave an absorbance corresponding to 3σ for the standard deviation of the fluctuation of the blank, and was 0.11 µg dm$^{-3}$ ($n = 5$) when 50 cm$^3$ sample solution was used.

To check the effectiveness of the present SPS method, the concentrations of total iron in water samples related to boiler system in a thermal power plant were determined, and the results were shown in Table 2. Although the total iron concentrations in all of the samples were very low (lower than 1 µg dm$^{-3}$), and the present method could determine the iron concentrations, indicating that the present method is possible to determine the iron at about 0.1 µg dm$^{-3}$ level. The cross-check results by ICP-MS of the total iron of these samples gave a fairly good agreement with the results obtained by the present method, confirming the accuracy and the effectiveness of the present method.

The samples were collected from three different sites in the thermal power plant, and were checked the time dependence fluctuation of the iron concentration at the same sites. The results of the A and C sites showed that there was a fluctuation of the iron concentration according to the sample collection time, indicating that there might be particulate iron in the sample. The fact was confirmed by the ICP-MS measurement of the samples on-site filtered through 0.45-µm membrane filters.
Table 2 Iron concentration of boiler water of a thermal power plant

<table>
<thead>
<tr>
<th>Site</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Collecting time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPS</td>
<td>0.3±0.1 (n = 3)</td>
<td>0.4±0.1 (n = 3)</td>
<td>0.3±0.1 (n = 3)</td>
</tr>
<tr>
<td>ICP-MS Total</td>
<td>0.00</td>
<td>0.61</td>
<td>0.28</td>
</tr>
<tr>
<td>Dissoled</td>
<td>0.00</td>
<td>-</td>
<td>0.02</td>
</tr>
</tbody>
</table>

- No ICP-MS result.

* Agilent Model 7500 cx at Kyushu Environmental Evaluation Association; measured against the internal standard of 89Y.
Conclusion

The present SPS method greatly improved the sensitivity of the TPTZ spectrophotometric method for total iron determination, and made it possible to determine the sub-µg dm$^{-3}$ level total iron in water samples without any special treatment and expensive equipment. The present method has several advantages compared to the already proposed methods as shown in Table 3. Compared to the TPTZ solution method (JIS method), the analytical time of present SPS method is much shorter because the time-wasting concentration of the sample by heating is saved; Compared to the AAS and ICP-MS method, the equipment of the present SPS method is much inexpensive, decreasing the cost of equipments and maintenance for the industries. The present method is useful for monitoring of iron in boiler systems of both nuclear and thermal power plants.

Table 3 Comparison of the present SPS method to other methods

<table>
<thead>
<tr>
<th></th>
<th>Present method</th>
<th>TPTZ solution method (JIS)</th>
<th>AAS</th>
<th>ICP-MS</th>
</tr>
</thead>
<tbody>
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<td>1</td>
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<tr>
<td>Equipment</td>
<td>low</td>
<td>low</td>
<td>high</td>
<td>high</td>
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<tr>
<td>Maintenance</td>
<td>low</td>
<td>low</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>Evaluation</td>
<td>○</td>
<td>∆</td>
<td>∆</td>
<td>∆</td>
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</tbody>
</table>
References


Introduction

Chromium exists in natural water in two different thermodynamically stable oxidation states, Cr(III) and Cr(VI). It is well known that Cr(III) is one of the essential trace elements for humans. A daily intake limit of 50 - 200 µg chromium is recommended by the US National Council. On the other hand, Cr(VI) is toxic to organisms due to its strong oxidation power. The WHO proposed limit for drinking water was regulated at 50 µg dm\(^{-3}\) for Cr(VI) in 1958, but was later changed to the regulation for total chromium because of the difficulties in speciation analysis of Cr(VI). Speciation analysis is very important in addition to total chromium determination, because the health effect of the chromium species differ from one another depending on their oxidation states. In addition, in the directives (Restriction of Hazardous Substances, RoHS) on use of several hazardous metals of the European Union, Cr(VI) was listed as a regulated item.

The modern instrumental techniques, such as ICP-AES and ICP-MS, flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS) are just for the determination of total concentrations, although they are well known as highly sensitive tools for the determination of trace elements. Consequently, the target species need to be separated and preconcentrated to realize speciation analysis.

The reported speciation methods for chromium usually includes coprecipitation and extraction (solvent extraction or solid-phase sorption) by batch method and retention of Cr(III) and/or Cr(VI) on a solid phase column followed by instrumental analysis. Among the various
methods, coprecipitation and extraction were the earlier reported methods, in which one species of Cr(VI) or Cr(III) was separated from the sample solution mainly by batch method. The other species was separated and determined by the same procedures after its reduction or oxidation. Although these methods could realize speciation analysis, the complex separation and preconcentration procedures require a large amount (25 - 200 cm$^3$) of sample, and the sensitivities (detection limit of 0.2 - 0.5 µg dm$^{-3}$ for Cr(III) and 0.03 µg dm$^{-3}$ for Cr(VI)) were sometimes insufficient to analyze real samples such as natural water.

In recent years, the most widely developed methodologies for the speciation of chromium in water samples are based on flow systems equipped with solid-phase columns that can retain Cr(III) and/or Cr(VI) and highly sensitive instruments. The two strategies involved are as follows: a) the species of Cr(III) or Cr(VI) was retained on the column, then eluted and instrumentally determined. The other species was separated and preconcentrated after its reduction or oxidation by batch method,$^{11,12}$ or were done reduction or oxidation in the flow system and retained on another column,$^{13}$ then instrumentally analyzed as the same manner as total chromium; b) Cr(III) and Cr(VI) were retained on two individual columns, then eluted and analyzed sequentially.$^{14}$ These methods greatly improved the sensitivity (the detection limits were 0.04 µg dm$^{-3}$ for Cr(VI) and 0.06 µg dm$^{-3}$ for Cr(III)) and simplified the procedures of chromium speciation methods. However, these methods included the use of sophisticated instruments, such as ICP-AES, which meant high costs for the determination. Spectrophotometry may be the best choice to decrease the cost of determination. In the leaching test described in the Restriction of Hazardous Substances (RoHS directives), the time-consuming and complex leaching procedures$^{15}$ are no longer needed if the sensitivity of the detection method is high enough to obtain a measurable concentration of chromium species in a short time by a simpler leaching procedure.
It is known that 1,5-diphenylcarbazide (DPC) selectively reacts with Cr(VI) under strongly acidic conditions, producing the Cr(III)-1,5-diphenylcarbazone (DPCO) complex (Fig. 1, 1:1 molar ratio);\textsuperscript{16,17} this complex is a divalent cation, and shows an absorption maximum at 540 nm. Cr(III) complexes are generally inert, and therefore, the produced Cr(III)-DPCO complex is not decomposed during chromatographic separation. Cr(III)-DPCO complex was reported to be stable for at least 24 h.\textsuperscript{18} DPC also reacts with other metallic ions to give DPCO complexes,\textsuperscript{19} but the complexes easily decompose under strongly acidic conditions. That is to say, the Cr(VI)-DPC reaction is highly selective under strongly acidic conditions.\textsuperscript{20} These properties make it possible to utilize a cation-exchange column as a reaction/concentration/separation medium in a high-performance liquid chromatography (HPLC) system; this idea was originally developed by my laboratory for the on-line trace analysis of boron using chromotropic acid as a complexing reagent.\textsuperscript{21} For the Cr(VI) determination method, the DPC has no absorption at 540 nm, at which the complex has strong absorption. DPC can be concentrated on a short column by hydrophobic interaction. Cr(VI) in the sample solution can be directly reacted with DPC on the column, and the resulting Cr(III)-DPCO complex will also be retained in the column by an electrostatic interaction and hydrophobic interaction. The DPC coloring reagent and the complex can be easily eluted by an effective eluent containing organic solvent and a multi-charged cation salt. Thus, possible dilution in the column can be avoided, and consequently, higher sensitivity is expected.

The aim of this work was to develop a highly sensitive and highly reproducible speciation analysis method for the trace analysis of chromium in water based to the procedure mentioned above. Some cation-exchange columns were examined for the concentration of DPC utilizing the hydrophobic interaction between the ion exchanger column and DPC. We employed the (a)
strategy for the speciation analysis of chromium, because it was found that the photo-oxidation of Cr(III) can be performed by ultraviolet (UV) irradiation without the presence of any additional oxidizing reagents.\textsuperscript{22} Cr(III) was on-line oxidized to Cr(VI) by a low-pressure ultraviolet (UV) lamp and then the total chromium could be directly measured using the same flow system. The proposed method allowed for high sensitivity and high precision without the use of any high-cost instruments.

\[ \text{Fig.1 Chemical reaction of Cr(VI) and DPC} \]

\section*{Experimental}

\textit{Chemicals}

All chemicals used were of analytical grade. Deionized water was prepared by a Milli-Q SP system (Millipore, USA) throughout the study.

The Cr(III) standard solution (0.10 mol dm\(^{-3}\)) was prepared by dissolving 25 g of chromium potassium sulfate dodecahydrate (Kishida, Osaka) in water and diluted to 250 cm\(^3\), and the Cr(III) concentration was determined by FAAS. The Cr(VI) standard solution for AAS (100 mg dm\(^{-3}\)) was purchased from Wako, Osaka, Japan. Hydrochloric acid (1.0 mol dm\(^{-3}\)) was prepared by diluting 21 cm\(^3\) of concentrated hydrochloric acid of super special grade (Wako, Osaka) with water up to 250 cm\(^3\). Sulfuric acid (2.5 mol dm\(^{-3}\)) was prepared by diluting 35 cm\(^3\) of concentrated sulfuric acid of super special grade (Wako) with water up to 250 cm\(^3\). A lanthanum
chloride (1.0 mol dm$^{-3}$) solution was prepared by diluting 37 g of lanthanum chloride heptahydrate (Wako) with water up to 100 cm$^3$.

The coloring reagent solution (DPC 2.0 mmol dm$^{-3}$, sulfuric acid 0.375 mol dm$^{-3}$) was prepared by diluting 0.048 g of DPC (Wako) in 15 cm$^3$ of the sulfuric acid (2.5 mol dm$^{-3}$) solution and diluted with water up to 100 cm$^3$, then filtered using a 0.45-µm PTFE membrane filter.

The carrier solution (sulfuric acid 0.01 mol dm$^{-3}$) was prepared by diluting 8 cm$^3$ of 2.5 mol dm$^{-3}$ sulfuric acid with water up to 2 dm$^3$.

The eluent solution was prepared by mixing 30 cm$^3$ of 1-propanol (99.5%, Wako), 2 cm$^3$ of 0.25 mol dm$^{-3}$ lanthanum chloride and 0.625 cm$^3$ of 4 mol dm$^{-3}$ hydrochloric acid with water up to 250 cm$^3$. The carrier and the eluent solutions were heated and degassed by an ultrasonic treatment before use.

**Apparatus**

Double-plunger pumps (DM2M-1024, SNK, Hamura, Tokyo) were used to pump the carrier solutions. Six-way rotary valves were used for the introduction of the coloring reagent and eluent. A double four-way rotary valve was used for the sample introduction. The column was a cation-exchange column for ion chromatography (TSK gel IC-Cation, 4.6 mm i.d., 10 mm long, Tosoh, Tokyo). Absorbance measurements were taken by using an SPD-10AV$_{VP}$ UV-VIS spectrophotometer (Shimadzu, Kyoto). A SIC µ7 data processor was used for recording the signal peak of the target complex. A low pressure mercury UV lamp (25 W, SUV 40 DH-12, Sen Lights Co., Osaka) was used for the photo oxidation of Cr(III) to Cr(VI).
**Analytical procedure**

The flow diagram for the determination of Cr(VI) is shown in Fig. 2. The carrier solutions 1 and 2 were pumped using double-plunger pumps A1 and A2, and the flow rates were set at 1.2 cm$^3$ min$^{-1}$ and 0.3 cm$^3$ min$^{-1}$, respectively. A water sample was first filled in one of the 3.9 cm$^3$ PTFE tubes (B1 or B2) attached to the PTFE double four-way valve with two PTFE tube loops (1 mm i.d., 5 m long). The water sample and 1.2 cm$^3$ of the coloring reagent solution were simultaneously introduced into the flow system from valves B and C. After the on-line coloring of Cr(VI) and the concentration on the column, 7.8 cm$^3$ of the eluent (12 (v/v) % 1-propanol including 2 mmol dm$^{-3}$ of LaCl$_3$ and 0.01 mol dm$^{-3}$ HCl) was introduced from valve D. The cation-exchange column was placed in a thermostated bath at 50°C. A UV-VIS detector for the HPLC was used and the absorbance of the Cr(III)-DPC O complex at 540 nm was continuously monitored by the SIC µ7 data processor. During the analysis of a sample, the next sample was introduced into the other sample tube loop.

For the total chromium determination, a water sample of which the pH was adjusted to 3.4 with sulfuric acid was pumped by the A3 pump (a peristaltic pump, Elela MP-A, Tokyo) and flowed through a quartz tube (1.0 mm i.d., 444 cm long) placed on the surface of the UV lamp with the flow rate set at 0.6 cm$^3$ min$^{-1}$, as shown in Fig. 3. In the quartz tube, Cr(III) was oxidized to Cr(VI) by UV irradiation. The dead volume of the oxidation system was 4.5 cm$^3$, and therefore, it was necessary to pump the sample solution for at least 16 min. After discarding the first portion for 8 min, the sample solution was collected for the Cr(VI) determination. The Cr(III) concentration was calculated by the difference in the values of the total chromium and Cr(VI).
Fig. 2  Schematic diagram of flow system for Cr(VI) determination.  1 and 2: carrier solutions (H$_2$SO$_4$ 0.010 mol dm$^{-3}$); A1 and A2: pumps, flow rate: 1.2 cm$^3$ min$^{-1}$ and 0.3 cm$^3$ min$^{-1}$, respectively; B1 and B2: PTFE double four-way valve with two PTFE tube loops (3.9 cm$^3$) for sample introduction; C: PTFE six-way rotary valve with PTFE tube loop (1.2 cm$^3$) for DPC introduction; D: PTFE six-way rotary valves with PTFE tube loop (7.8 cm$^3$) for eluent introduction; E: cation-exchange column for ion chromatography, TSK gel IC-Cation (4.6 mm i.d., 10 mm long); F: UV-VIS detector for HPLC (SHIMADZU SPD-10AV$_{vp}$)

Fig. 3 Schematic diagram of photo oxidation system.  UV lamp surrounded by 12 quartz tubes (1.0 cm i.d., 37 cm long) connected to each other by PTFE tubing; A3: Peristaltic pump, flow rate: 0.6 cm$^3$ min$^{-1}$. 

44
Results and Discussion

Column for the retention of DPC and the complexation

DPC is scarcely soluble in water, and therefore, the hydrophobic interaction between the DPC and cation exchanger is very important from the viewpoint of producing a locally high concentration area in the column to promote the Cr(VI)-DPC reaction. Some packed columns have been examined for the concentration and separation of DPC and the DPCO-Cr(III) complex in a Master Thesis of my lab. Finally, the cation-exchange column employed in this study was a strong-acid type with sulfo groups, commercially available for ion chromatography as TSK IC-Cation (Tosoh), a packed column of cross-linked poly(vinyl alcohol). The distribution ratio of DPC between the resin and 0.01 mol dm$^{-3}$ of sulfuric acid was 4.5 cm$^3$ g$^{-1}$. For the Cr(III)-DPCO complex, the distribution ratio was greater than $10^4$ cm$^3$ g$^{-1}$. Since the retention of DPC on the TSK gel IC-Cation column is low, the DPC solution was simultaneously introduced into the column when the samples were introduced, and the DPC concentration in the column was maintained at a concentration about five times higher than that in solution.

In the ion chromatography method developed by Padarauskas et al., the color developing reaction of Cr(VI) and DPC was completed by a batch method using a large amount of sample (100 cm$^3$), and then the solution was loaded onto a preconcentration column ($C_{18}$-bonded silica column, 50 × 6 mm) for 20 min. After the preconcentration step, the analysis of the sample was performed by connecting to another column ($C_{18}$ 10 × 6 mm) and eluting the complex with an eluent containing $6 \times 10^{-3}$ mol dm$^{-3}$ sulfuric acid and 20% (v/v) acetonitrile. The reaction rate of Cr(VI) and DPC was significantly higher under the strongly acidic condition. However, the mobile phase of which the pH value was lower than 2 can cause degradation of the $C_{18}$-bonded
silica column. Therefore, the lower acid concentration mobile phase was used in their study, resulting in a longer analysis time (longer than 30 min), which made the method impractical for common applications. The present method could avoid such a problem by using the TSK gel IC-Cation column. A schematic diagram of the on-line reaction/concentration/separation method for the Cr(VI)-DPC reaction is shown in Fig. 4.

![Diagram](image)

Fig. 4 Outline of the processes of concentration and separation of the Cr(III)-DCPO complex by a cation-exchange column. Green: DPC; Pink: DPCO-Cr(III) complex. (a) Introduction of DPC and sample solution into the flow line: DPC and the sample containing Cr(VI) were simultaneously introduced into the flow system from the different loops and mixed in the flow tube. The reaction started as soon as the Cr(VI) and DPC were mixed. (b) DPC concentration and the Cr(III)-DPCO complexation in the column: The mixed solution reached the column and both the DPC and DPCO-Cr(III) complex were concentrated on the column. The concentrated DPC made it possible for the remaining Cr(VI) to completely react with the DPC on the column in a very short time. (c) Separation and elution of the Cr(III)-DCPO complex: DPC was sorbed on the column by a hydrophobic interaction. The divalent cation complex was sorbed in the column by an electrostatic interaction and hydrophobic interaction. The absorbed complex and remaining DPC were eluted by a mixed solution in a short time and the peak of the generated complex was detected.
Optimization for Cr(VI) determinations

The effects of DPC concentration, sulfuric acid concentration, and temperature on the formation of DPCO-Cr(III) complex were discussed in the Master thesis of Mr. Ashitomi. The DPC concentration of the coloring reagent stock solution was fixed as 2.0 mmol dm$^{-3}$, sulfuric acid concentration of the DPC coloring reagent was optimized to 0.075 mol dm$^{-3}$, and the temperature of the column was maintained at 50°C.

**Length of the mixing coil.** The DPC was mixed and reacted with the sample solution in the PTFE tube after the introduction. The effect of the length of the mixing tube on the peak area of the DPC-Cr(III) complex is shown in Fig. 5. When the mixing tube was longer than 5 m, the peak areas were almost the same. The result indicated that the complexation in the resin phase was not sufficient and the on-line reaction in the 5 m mixing tube was required for the complete reaction.

**Eluent composition.** The Cr(VI)-DPC complex interacts with the cation exchanger resin by an electrostatic interaction and hydrophobic interaction. Therefore, a mixed organic solvent containing a metal cation is effective to elute the complex from the column. Because of the higher selectivity coefficient, trivalent cations were considered to be used as an eluent. Among common cations, Fe(III) reacts with DPC to produce a red color complex; Al$^{3+}$ has a fairly low selectivity coefficient; consequently, La$^{3+}$ was chosen as a component of the eluent. Therefore, a mixture of 1-propanol and a lanthanum chloride solution containing 0.01 mol dm$^{-3}$ HCl was used as the eluent to elute the complex from the column. It is well known that the concentration of the eluent affects the retention time and peak area of the target complex. Both the concentrations of 1-propanol and lanthanum chloride were checked to obtain the optimum conditions. The lanthanum chloride concentration of 1 - 10 mmol dm$^{-3}$ and 1-propanol concentration of 10 - 15% (v/v) were examined, and the results are shown in Fig. 6. A higher concentration of lanthanum
chloride made the retention time shorter, and the peak area narrower. For 1-propanol, the concentration effect on the retention time was the same as that for the lanthanum chloride. However, the effect on the peak area was different, because of the overlapping with the solvent peak, the peak area of the target complex was smaller at the higher concentration of 1-propanol. Considering the peak area and the resolution of the solvent peak from the target peak, the eluent concentration was fixed at 2 mmol dm$^{-3}$ lanthanum chloride and 12% 1-propanol.
Fig. 5  Effect of the length of the mixing tube on the peak area of Cr(III)-DPCO complex.
Cr(VI) concentration: 5 µg dm$^{-3}$; volume: 1.1 cm$^3$.

Fig. 6 Effect of eluent concentration on the peak area and retention time.  
(a) Cr(VI) 1 µg dm$^{-3}$, 1-propanol 15%; (b) Cr(VI) 1 µg dm$^{-3}$, LaCl$_3$ 2 mmol dm$^{-3}$
Effects of coexisting ions

The interferences of coexisting ions on the Cr(VI) determination were examined and discussed in Mater Thesis of Mr. Ashitomi, and the results were shown in his thesis. Since V(V) and Mo(VI) are oxidants and consume DPC, the Cr(VI)-DPC reaction was affected, but the effect was fairly small, even if the concentration ratio to Cr(VI) was 2000. Mn(II) and Cr(III) gave positive errors on the Cr(VI) determination caused by the complexation of the ions with the DPC or DPCO. However, the effects were slight even if the concentration ratio to Cr(VI) was greater than a few hundred. Fe(III) and Cu(II) had a negative effect on the Cr(VI) determination. Although the detailed reaction mechanism is unclear, Cu(II) was reported to catalyze the oxidation of DPC by dissolved oxygen. In the case of Fe(III), Fe(III) catalytically affects the Cr(VI) determination; Fe(III) oxidizes DPC to DPCO, and the resulting Fe(II) is oxidized by Cr(VI) or dissolved oxygen to form Fe(III), and the Fe(III) reacts with DPC again. The influence of these ions can be ignored, because their concentrations in natural water are at µg dm$^{-3}$ levels. Other common solutes, such as Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, NO$_3^-$, PO$_4^{3-}$, SO$_4^{2-}$, B(OH)$_3$ and Si(OH)$_4$ have no interferences for the determination of Cr(VI) by DPC method.
Speciation analysis of trace chromium

If the dissolved Cr(III) could be quantitatively oxidized to Cr(VI), the determination of total chromium was attained by the present method, that is to say, the method has made it possible to do the speciation analyses of chromium. Taguchi et al. reported that the photo-oxidation of Cr(III) to Cr(VI) by the ·OH radical formed during the irradiation of vacuum ultraviolet rays could be applied to the successive determination of Cr(VI) and total chromium by FIA.\(^{22}\) Therefore, the photo oxidation of Cr(III) using an ultraviolet lamp was first examined.

Oxidation of Cr(III) using a photo (ultraviolet) oxidation system. The flow system for the photo oxidation of Cr(III) is shown in Fig. 3. A sample solution containing Cr(III) and 0.2 mmol dm\(^{-3}\) \(\text{H}_2\text{SO}_4\) at pH 3.4 was introduced into a quartz tube surrounding the UV lamp radiating 185-nm light. Chromium(III) was quantitatively oxidized to Cr(VI) by the ·OH radicals formed during the UV irradiation when the solution flowed through the quartz tube.\(^{22}\) After being oxidized, the solution was introduced into the Cr(VI) determination flow system from valve B. Therefore, the total chromium (Cr(VI) + Cr(III)) was determined at the detector and the speciation analysis of Cr(III) and Cr(VI) was easily performed.

Effect of pH. The effect of the sulfuric acid concentration on the photo oxidation of Cr(III) was investigated. A series of sample solutions (containing 1 \(\mu\)g dm\(^{-3}\) Cr(III)) were prepared at different sulfuric acid concentrations from \(5 \times 10^{-3}\) to \(5 \times 10^{-7}\), and then Cr(III) was oxidized to Cr(VI) by the UV lamp and determined by the present Cr(VI) determination method. At pH 2, no Cr(VI) was detected, suggesting that no Cr(III) was oxidized. At a pH higher than 2, the extent of oxidation increased with increasing pH, and reached a maximum at pH 3.4. The extent of the oxidation then gradually decreased. The OH-Cr(III) redox reaction is expressed by Eq. (1).\(^{24,25}\)

\[
\text{Cr}^{3+} + 3 \cdot \text{OH} + \text{H}_2\text{O} = \text{HCrO}_4^- + 4 \text{H}^+ , \quad E^o = 1.00 \text{ V}
\]  

\(^{24,25}\)
In the equilibrium state at 25°C, Eq. (2) can be obtained using the Nernst equation of reaction (1).

\[
\log \left( \frac{([HCrO_4])}{([H^+])([Cr^{3+}](·OH)^3)} \right) = 50.8
\]

(2)

where the bracket denotes the activity of each species. Eq. (2) shows that reaction (1) is pH dependent and the results in the lower pH range in Fig. 7 could be explained if \(·OH\) = 10\(^{-20}\) mol dm\(^{-3}\), \(i.e.,\) \(\frac{([HCrO_4])}{([Cr^{3+}])} = 10^{1.2}\) at pH 2 and 10\(^{2.8}\) at pH 3. Although the \(·OH\) lifetime is very short,\(^{26}\) the \(·OH\) radicals are continuously generated by UV lamp irradiation. Therefore, the calculated \(·OH\) concentration may be that of the steady state. In the higher pH range, the predominant species\(^{27}\) of Cr(III) are Cr(OH)\(^{2+}\) and Cr(OH)\(_2^+\), the decrease in the extent of oxidation may be due to the hydrolysis of Cr(III), and therefore, the active species participating in the oxidation by \(·OH\) is Cr\(^{3+}\).\(^{22}\)

**Effect of irradiation time.** The irradiation time differed for the samples containing different amounts of organic matter. For the highly purified water solution, the irradiation time of 1.6 min was enough to quantitatively oxidize Cr(III) to Cr(VI), as shown in Fig. 8. For the water samples containing high amounts of organic matter, a longer irradiation time was necessary. Fig. 8 also shows the result of a water sample from the Muromi River, Fukuoka, Japan. The dissolved organic carbon (DOC) concentration of the water sample was 0.8 mg dm\(^{-3}\). I can think of two possible reasons for the slow oxidation. The organic matter may have formed complexes with the chromium species and prevented the oxidation. On the other hand, since the concentration of organic matter was obviously higher than the concentration of chromium, it may be that the \(·OH\) radicals were consumed by the oxidation of the organic matter and the extent of oxidation of Cr(III) to Cr(VI) was reduced. The present study showed that the irradiation time of 8 min was enough for the oxidation of the water samples that contained organic matter of less than 1 mg dm\(^{-3}\).
Fig. 7 Effect of pH on the oxidation ratio. Cr(III) concentration: 1 µg dm$^{-3}$.

Fig. 8 Effect of the irradiation time on the oxidation of Cr(III). ●: highly purified water, Cr(III) concentration: 1 µg dm$^{-3}$; ○: river water from Muromi River, Fukuoka, Japan, 28$^{th}$, Dec. 2012, TOC: 0.8 mg dm$^{-3}$, spiked Cr(III) concentration: 0.2 µg dm$^{-3}$
Detection limit, precision and accuracy

An example of the chromatogram obtained using the HPLC system is shown in Fig. 9. The calibration curve plotted between the peak area of the complex versus the Cr(VI) concentration was linear in the range of 0.001 - 100 µg dm$^{-3}$ Cr(VI) with a correlation coefficient of 0.999. For the Cr(VI) determination, the detection limit is defined as the concentration that gives an absorbance corresponding to 3σ for the standard deviation of the fluctuation of the blank, and this limit was 0.6 ng dm$^{-3}$ ($n = 5$) when using a 3.9 cm$^3$ sample solution. The Cr (VI) analysis time was 8 min and the sample volume was 3.9 cm$^3$. In comparison to the method of Padarauskas et al.,$^{20}$ the present method was simpler, time-saving and highly sensitive, and can be used for various applications, especially for ultratrace chromium determinations. For the total chromium determination, the detection limit of the proposed method was 0.8 ng dm$^{-3}$ ($n = 5$).

To check the precision of the present speciation analysis method, the concentrations of Cr(VI) in three water samples were determined. The water samples were collected from the city water of Fukuoka, well water of Kyushu University’s Hakozaki campus, and river water from the Experimental Forest of Kyushu University, Sasaguri, Fukuoka. The results were 0.10 ± 0.02 µg dm$^{-3}$ ($n = 4$), 1.38 ± 0.02 µg dm$^{-3}$ ($n = 4$) and 2.33 ± 0.01 µg dm$^{-3}$ ($n = 3$), respectively. The proposed method allows one to determine Cr(VI) in the samples with high precision. Among the samples, the total chromium concentration of the river water sample was also determined by connecting the photo oxidation system and Cr(VI) determination system, and the result was 2.45 ± 0.01 µg dm$^{-3}$ ($n = 3$). The cross-check result by ICP-MS of the total Cr of this sample was 2.54 µg dm$^{-3}$. The results were in fairly good agreement with one another, strongly confirming the effectiveness of the present method.
In order to check the recovery of the Cr(VI) and the total Cr, the standard addition method was carried out for the well water and the river waters, and the results are listed in Tables 1 and 2. For the total chromium determination, Cr(VI) in the samples was first reduced by the dissolved organic compound under an acidic condition (sulfuric acid 0.01 mol dm$^{-3}$) before the photo oxidation. All the recoveries were between 95 - 104% with high precision. Noticeably, the hardness of the well water was over 180 mg dm$^{-3}$. It is clear that the recovery for each sample solution was acceptable and the results showed that the proposed system did not suffer from any other interferences.

Fig. 9 Chromatograms of Cr(III)-DPCO complex under the optimum conditions. Sample 3.9 cm$^3$; 1: 0.2 µg dm$^{-3}$, 2: 10 ng dm$^{-3}$ Cr(III). After introduction of the eluent, the baseline was reduced due to the change in the composition from the carrier to the eluent. The complex peak was then observed. It took about 8 min for each measurement.
### Table 1 Recovery test of Cr(VI) determination for water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added Cr(VI) / µg dm(^{-3})</th>
<th>Found Cr(VI) / µg dm(^{-3})</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well water (2 × dilution)</td>
<td>0</td>
<td>0.71</td>
<td>---</td>
</tr>
<tr>
<td>((n = 1))</td>
<td>1.0</td>
<td>1.73</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>2.79</td>
<td>104</td>
</tr>
<tr>
<td>River water (3 × dilution)</td>
<td>0</td>
<td>0.78 ± 0.01</td>
<td>---</td>
</tr>
<tr>
<td>((n = 3))</td>
<td>0.17</td>
<td>0.95 ± 0.00</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>1.29 ± 0.01</td>
<td>102</td>
</tr>
</tbody>
</table>

Well water: hardness of the water was over 180 mg dm\(^{-3}\), and the pH was 8.16 (17.6 °C, January 10, 2012); River water: pH 7.94 (18.5°C, May 11, 2012).

### Table 2 Recovery test of total Cr determination of water sample \((n = 2)\)

<table>
<thead>
<tr>
<th>Added Cr(III) / µg dm(^{-3})</th>
<th>Found / µg dm(^{-3})</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.035, 0.034</td>
<td>-</td>
</tr>
<tr>
<td>0.202</td>
<td>0.226, 0.225</td>
<td>95</td>
</tr>
<tr>
<td>0.395</td>
<td>0.416, 0.418</td>
<td>97</td>
</tr>
</tbody>
</table>

Conclusion

The results of the Cr(III) and Cr(VI) dissolved in natural water obtained by the proposed method could be applied to the study of dissolved chromium speciation in natural water. The present speciation analysis result (pH 7.94, total Cr 2.45 µg dm\(^{-3}\), Cr(VI) 2.33 µg dm\(^{-3}\)) of the river water from the Experimental Forest of Kyushu University, Japan, indicated that Cr(VI) was predominant in the weakly alkaline river water. This conclusion was consistent with the result of the previous study.\(^{28}\)

The proposed method has the flexibility to obtain higher sensitivity by changing the sample volume if necessary. The analysis of one sample can be finished in just a short time, and the whole experimental system is simple and inexpensive. Based on our results, the proposed method is the most sensitive among the various reported methods, including ICP-AES and ICP-MS. A comparison of the present method with the reported so far speciation methods is shown in Table 3.

This method is applicable to various purposes, especially for the speciation analysis of ng dm\(^{-3}\) levels of chromium. In addition, the proposed strategy will be broadly applicable to the various reaction systems of trace elements.

<table>
<thead>
<tr>
<th>Detection</th>
<th>Sample volume / cm(^3)</th>
<th>DL / µg dm(^{-3})</th>
<th>Analytical time / min</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cr(III)</td>
<td>Cr(VI)</td>
<td>Cr(III)</td>
</tr>
<tr>
<td>Spectrophotometry</td>
<td>100</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>0.1</td>
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<td>30</td>
<td>5</td>
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<tr>
<td>ICP-MS</td>
<td>0.1</td>
<td>0.35</td>
<td>0.20</td>
<td>8</td>
</tr>
<tr>
<td>Spectrophotometry</td>
<td>3.9</td>
<td>0.0008</td>
<td>0.0006</td>
<td>24</td>
</tr>
</tbody>
</table>

This method is applicable to various purposes, especially for the speciation analysis of ng dm\(^{-3}\) levels of chromium. In addition, the proposed strategy will be broadly applicable to the various reaction systems of trace elements.
References


Chapter 2. Speciation analysis of dissolved chromium leached from stainless steel by on-line reaction/concentration/separation method

Introduction

Stainless steel (SS) is greatly produced and widely used for various applications all over the world since it does not readily corrode or rust with water and in humid air as ordinary pure metal materials do because of a passive layer on the surface. As SSs are composed of several metals, and releases the metals under certain conditions, human beings are likely to be exposed to the released metal ions dissolved under certain conditions. Therefore, above facts attract the attentions of researchers in various fields. Chromium is contained at least 10.5% by mass as one of the major components, and makes SSs corrosion resistant. Many researchers have reported the leaching of chromium from SS products and the waste of the SS industries. However, there have been few reports on the speciation analysis of Cr leached from SS. It is known that Cr(III) is one of the essential trace elements. However, Cr(VI) is toxic to organisms due to the strong oxidation power. Therefore, the speciation analysis is very important. A highly sensitive, simple and highly-reproducible flow method for speciation analysis of ultratrace Cr(VI) and Cr(III) leached from SS has been successfully developed by utilizing a cation-exchange column as a reaction/concentration/separation medium in an HPLC system in my laboratory as described in Chapter 1 in Part 2. The Cr(III) could be on-line oxidized to Cr(VI) using a UV photo oxidation system and then measured by the proposed method as total chromium. In this chapter, the application of the method for the speciation analysis of leached Cr(III) and Cr(VI) from the stainless steel is reported.
Experimental

Chemicals and Apparatus

All reagents and apparatus used for determination of chromium were the same as described in Chapter 1.

The stainless steel powder (SUS304, 100 mesh Ni 8%, Cr 18%, Fe 75% (W/W)) and panels (SUS304, Cr 18%, Ni 9%, 0.1 × 100 × 300 mm; SUS631, Cr 17%, Ni 7%, 0.1 × 100 × 300 mm) were purchased from Nilaco (Tokyo).

Analytical procedure

The SUS304 stainless-steel powder (1 g, 100 mesh) was added to 20 cm$^3$ of water and shaken for a fixed time. The solid powder was then filtered and the Cr(VI) and total chromium were determined by the developed chromium determination method described in Chapter 1.

The SUS304 panel (Cr 18%, Ni 9%, 0.1 × 100 × 300 mm, previously degreased in surfactant agent solution (2% dcn 90, AR, BROWN Co.)) and the SUS631 panel (Cr 17%, Ni 7%, 0.1 × 100 × 300 mm, previously degreased in acetone) were folded into rectangle shape and put in a PE bottle, then added by 300 cm$^3$ highly purified water. The mixture was shaken in a thermostat bath (25°C), and water samples were taken periodically for the speciation analysis of Cr by the same method. All of the samples were filtered through a 0.20 μm membrane filter before the determination.
Results and Discussion

Leaching of Cr from SUS304 powder

The leaching results of Cr(III) and Cr(VI) from SUS304 stainless-steel powder are shown in Fig. 1; both Cr(III) and Cr(VI) were detected in the leachate. The concentration of Cr(III) leached in 2 hrs was around 1 µg dm$^{-3}$, and Cr(VI) was 42 ng dm$^{-3}$, indicating that the predominant species leached from stainless-steel was Cr(III). For both Cr(III) and Cr(VI), during the initial 20 min, there was a rapid increase in the concentrations. It was possible that there existed soluble chromium species on the surface of the stainless-steel since there was no special treatment of the stainless-steel sample before the leaching test. From 20 min to 2 h, the leached concentration of Cr(III) was almost linear with the time. The reaction rate was constant and could be considered as a zeroth-order reaction as follows: $[\text{Cr(III)}] = k t + c$, where $k$ is the rate constant and $c$ is the concentration of Cr(III) at $t = 0$. The linear regression equation gave $k = 0.0059$ µg dm$^{-3}$ min$^{-1}$ and $c = 0.35$ µg dm$^{-3}$. The leached concentration of Cr(VI) was not on a straight line even after 20 min. The result could be well explained by the zeroth-order reaction depending on the large excess but increasing Cr(III) concentration as follows: $[\text{Cr(VI)}] = 1/2 k' k r^2 + k' c t + c'$, where $k'$ is the rate constant of Cr(III) oxidation and $c'$ the Cr(VI) concentration at $t = 0$. The reaction rate was 0.36 ng dm$^{-3}$ min$^{-1}$ during the experimental time. This result indicated that the Cr(VI) in the leachate was derived probably from the oxidation of Cr(III) by the dissolved oxygen in the solution.
Fig. 1 Leaching of Cr(III) and Cr(VI) from SUS304 stainless-steel powder.
Leaching of Cr from SUS631 panel

The speciation analysis results of the Cr(III) release from SUS631 for 12 hrs are shown in Fig. 2. A similar leaching tendency with the SUS304 powder showed that at the beginning of the experiment, there was a rapid increase in Cr concentration: there were easily soluble components of Cr on the surface of the panel. Then, from 1 h to 12 h, the leached concentration of Cr(III) was increased almost linearly with time. As in the same way with SUS304, the reaction rate was constant and the reaction could be considered to be zeroth-order as follows: 

\[ [\text{Cr(III)}] = k t + c, \]

where \( k \) is the rate constant and \( c \) is the leached amount of Cr(III) at \( t = 0 \). The linear regression equation gave \( k = 0.0039 \, \mu g \, m^{-2} \, h^{-1} \) and \( c = 0.14 \, \mu g \, m^{-2} \). The leaching rate of Cr(III) from the panel was much lower than the rate of powder, probably due to the smaller surface area.

Fig. 3 showed the Cr(VI) leaching result from SUS631 panel. The detected Cr(VI) concentration gave a good agreement with the calculated concentration using the oxidation rate constant obtained by the experimental using SUS304 powder. This result confirmed the former result obtained from the SUS304 type powder. Regardless to the sample shape, the leaching of Cr(III) is linear with time, and Cr(VI) was from the oxidation of Cr(III) in the solution by the dissolved \( O_2 \).
y = 0.0039x + 0.1443
$R^2 = 0.9294$

Fig. 2 Leaching of Cr(III) from SUS631 stainless-steel panel.

Fig. 3 Leaching of Cr(VI) from SUS631 stainless-steel panel.
Leaching of Cr from SUS304 panel

A quite different phenomenon was observed for this experiment compared to the former two. In Fig. 4, the pink curve shows the time-dependent amounts of the dissolved Cr(III) in the original solution (filtered just after collected, and then oxidized by UV), and the blue one that of the total Cr(III) including dissolved Cr(III) and some suspended particles. In the latter case, the sample was irradiated without filtration, and the higher Cr(III) concentration was observed. The results indicated that at the beginning there were oxides or hydroxides particles (size >0.20 µm) on the surface of the SUS304 panel, then they dissolved into Cr(III) mononuclear species later. The reason might owe to the degreasing procedure. The SUS304 panel was degreased in surfactant agent 2% dcn solution, which is a highly alkaline solution (pH 12). Therefore, it was possible for some Cr-containing particles to be released and adsorbed on the surface of the SS panel. When the panel was put into water, these particles left from panel surface and dissolved in the water. The other possibility was that the high concentration of OH− attacked the surface of SUS304 panel and made the surface rougher than normal. There may be a very big change in the surface structure in strong alkaline solution. The Cr(VI) concentration was hard to be explained by the oxidation rate constant as shown in Fig. 5. Further study is needed for understanding of the mechanisms of surface change in strong alkaline solution. However, the result of this experiment indicated that the environmental condition is a major influence factor for the leaching mechanism of chromium from stainless steel.
Fig. 4 Leaching of Cr(III) from SUS304 stainless-steel panel.

Fig. 5 Leaching of Cr(VI) from SUS304 stainless-steel panel.
Conclusion

The results of the leaching test showed that the speciation analysis method developed in Chapter 1 can also be used without any difficulty in understanding the mechanism of the chromium leaching from various stainless-steel products.

The method used in this study can be applied to various fields in which chromium should be determined, such as the evaluation of environmental pollution potential, regulation of stainless-steel waste management, and the inspection of imported and exported chromium-containing products, since a short leaching time is sufficient to obtain a detectable concentration of the chromium leachate because of the high sensitivity. It made the leaching procedure even simpler than the RoHS standard extraction method.  

6
References


Conclusion

Generally, for evaluation of the environmental condition, large numbers of samples are needed. Nowadays, the sophisticated equipments and methods, such as ICP-MS and AAS, are very popular to analyze the large numbers of samples because of the sensitivity and convenience. However, such equipments only can provide the information about the total concentration of the chemical species, and the cost for the equipments and the daily maintenance are fairly high. With the increase of the interest of researchers on the detailed information of the existing species of the elements, and the increase of the desire for developing much greener and less consumption equipments of the whole society, the development of very effective, simple, and low-cost methods is an inevitable trend, and certainly, these methods should be applicable to the speciation analysis.

As a novel methodology, SPS successfully expanded the application of solid phase to micro and speciation analysis of trace chemical species in water samples. The most prominent contribution of SPS to the analytical chemistry is that SPS greatly improved the determination sensitivity for various target species because of the high volume ratio of sample solution and the solid phase, without any other complicated preconcentration process of sample solution. The compact spectrophotometer developed in our lab is very simple and inexpensive, and even LEDs could be developed as the light source for the spectrophotometer in this study, which was a great improvement for the on-site speciation analysis of the unstable species (i.e., Fe(II) in oxic condition) in natural water. The most important advantage is that the SPS method is easy useful for the speciation analysis of chemical species according to the coloring reactions specific to a target species. Therefore, the SPS method is widely applicable to the speciation analysis of large numbers of environmental samples, especially for the samples collected far away from the lab
room as in Inner Mongolia, storing the samples for long-time is possible to cause the transformation between the species.

The application of solid phase as a concentration/separation/reaction medium as described in the Part 2 of this thesis even improved the sensitivity of the speciation analysis of chemical species. Cr(VI) exists at ng dm$^{-3}$ level in natural water could be detected by this method without any pretreatment for the samples. Moreover, the application of the UV irradiation for the oxidation of Cr(III) to Cr(VI) could avoid the effect of Cr(III)-organic compounds on the determination of total chromium, since the UV irradiation decomposes the organic matters in water samples. The quantitative information of both Cr(VI) and Cr(III) can easily be obtained with high precision by this method, which can not been realized by the conventional methods such as ICP-MS. The developed method could be successfully applied for the speciation analysis of chromium at ng dm$^{-3}$ level leached from stainless steels, indicating that the method used in this study also can be applied to the various fields in which chromium should be determined, such as the evaluation of environmental pollution potential, regulation of stainless-steel waste management, and the inspection of imported and exported chromium-containing products (i.e., leather, and stainless steel), since a short leaching time is sufficient to obtain a detectable concentration of the chromium because of the high sensitivity.

Both methods can be used for the analysis of environmental samples in Inner Mongolia. It is hopeful to attract many attentions in analytical chemistry field in Inner Mongolia because of their effectiveness to the determination of real samples, and also hopeful to obtain more very valuable information of environmental conditions in Inner Mongolia.
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