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Flow injection analysis combined with a hydrothermal flow reactor: Application to kinetic determination of trace amounts of iridium using a water-soluble porphyrin

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ABSTRACT

A new type of flow injection analysis (FIA) system combined with an extremely high temperature reactor, namely hydrothermal flow injection analysis (HT-FIA), has been successfully constructed for the first time. Fundamental characteristics of HT-FIA system, such as limit temperature, pressure, and flow rate, were examined as an analytical tool. To demonstrate the potential of HT-FIA, the catalytic activity of Ir(IV) for the degradation of a water-soluble porphyrin, 5,10,15,20-tetraphenyl-21H,23H-porphinetetrasulfonic acid (TPPS), was applied for the determination of trace amounts of Ir(IV). Although the indicator reaction is very slow at room temperature, HT-FIA system enables to accelerate the reaction. A linear calibration curve was acquired at 10^{-8} M level of Ir(IV) and the interferences of platinum group metal ions were examined. The detection limit of Ir(IV) was 5.8×10^{-9} M and a fairly high-throughput analysis, of which more than 30 samples can be analyzed within 80 min, was achieved.

1. Introduction

The benefits and practicality of flow injection analysis (FIA) [1,2] are being recurrently acknowledged to develop sensitive and reproducible analytical methods by a couple of reasons [3] although FIA might be considered as somewhat a low technology as comparing to miniature analytical instruments, such as on-chip devices. First, the background of FIA is robust since the fundamental and practical researches to have been adequately carried out for many years. Second, FIA systems can be promptly constructed for different purposes using relatively low cost instruments, which is suitable from the viewpoint of the environmental harmless technology. Third, FIA possesses still advantages regarding small sample size, high throughput, and capability of automation in particular field, especially for miniature devices are hardly applied, such as non biological applications.

On the other hand, high temperature and pressure liquid phase reactions are becoming important in both fundamental and practical fields, such as, industrial chemical reactions, geochemical reactions, inorganic synthesis, life science [4–7]. High temperature reactions in aqueous solutions sometimes exhibit unique features as comparing to low temperature reactions. In particular, the acceleration effect of reactions at high temperatures is important. For instance, a reaction is more than 10^8 times accelerated with increasing temperature from 25 °C to 300 °C for the case that the reaction is accelerated 2 times by increasing of temperature 10 °C. In addition, the physical nature of aqueous solutions, such as the dielectric constant, is notably changed. If the temperature effects can be used for various analytical reactions, several advantageous would be expected while side reactions are needed to take into account. For instance, the temperature effect can be used for acceleration of the reactions instead of catalysts and the change of the nature of aqueous solutions would results in high selectivity of the target analytical reactions.

We have carried out investigations of hydrothermal flow reactor systems for monitoring high temperature liquid phase reactions [8,9]. The hydrothermal flow system consisting of a pump, a sample injector, a high temperature reactor, a pressure regulator, and a detector enables real-time and/or *in situ* monitoring at temperatures up to 400 °C at 50 MPa within the reaction time scale of 0.002–200 s, where UV–vis absorption spectra within 200–600 nm can be obtained for *in situ* monitoring of reactions. The hydrothermal flow reactor is based on invention of principle and techniques to control the residence time of samples at the high temperature and pressure reactor using very narrow tubing.

Although implementations that a high temperature reactor is incorporated into FIA have not been carried out, such applications would provide several advantages as a variation of FIA, such as acceleration of target analytic reactions, enhancement of selectivity of the target analytical reaction to side reactions, high throughput

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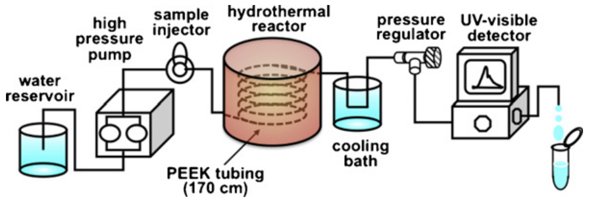

Fig. 1. Flow injection analysis system with hydrothermal flow reactor.

for analysis because of high-speed reactions. In addition, recently we have found that several chromogenic reagents are fairly stable at temperatures over 100 °C [10]. This fact indicates that many of the chromogenic reagents can be used and would profit readily the acceleration of target reactions using a high temperature reactor, although most of FIA systems should have been used at temperatures below 100 °C.

In the present study, the degradation of a water-soluble porphyrin, 5,10,15,20-tetraphenyl-21H,23H-porphinetetrasulfonic acid (TPPS), with oxidizing agent in the presence of a trace amount of platinum group metal ions, such as Ru(III) and Ir(IV) was focused [11]. In the previous study, the catalytic effect of Ru(III) was applied for the determination of 10^{-10} M level of Ru(III) ions without using FIA system, where the catalytic reactions are very slow so that the acceleration of these reactions would be definitely useful.

In the present study, a new FIA system attached with a high temperature reactor (HT-FIA) was set up for the first time. Second, the behaviors of the catalytic activity of Ir(IV) for the decomposition of TPPS with $NaIO_4$ were investigated and the analytical conditions for the determination of Ir(IV) were optimized by using HT-FIA [12].

2. Experimental

2.1. Reagents and apparatus

TPPS was purchased from Dojindo Laboratories (Japan). Standard solutions for 1000 ppm of Pt(IV), Pd(II), and Rh(III) ions were obtained from Wako Pure Chemicals Industries Ltd., Japan and those of Os(III), Ru(III), and Ir(IV) were obtained from Mitsuwa Chemical Co. Ltd., Japan. All other reagents used were purchased from Wako Pure Chemicals Industries Ltd., Japan as analytical grade.

A Shimadzu UV-1700 double-beam spectrophotometer with 1 cm quartz cells was used for measurements of absorbance and absorption spectra. A Horiba M-12 pH meter was used for the pH measurements.

2.2. Hydrothermal FIA

The set up of a hydrothermal FIA system was based on the real-time monitoring system for hydrothermal reactions described in the previous study [8–10]. The system consisted of a solvent reservoir, a high-pressure pump (LC-10AD, Shimadzu Corporation, Japan), a high-temperature reactor, a 0.1-mL loop injector or an auto sampler (AS-950-10, JASCO Corporation, Japan), a temperature controller, a back-pressure regulator (P-880, Upchurch Scientific), a UV–vis detector (L-7420, Hitachi High-Technologies Corporation, Japan), and a data integrator (D-7500, Hitachi High-Technologies Corporation, Japan) or (ADL-2020, LCScience, Japan) (Fig. 1). The UV–vis detector was attached at the downstream of the pressure regulator. The high-temperature reactor consists of heating blocks and PEEK tubing (Ø: 0.25 mm, 170 cm), which was possible to use at temperatures up to 250 °C within ±0.2 °C at a pressure up to 15 MPa. Distilled water in the solvent reservoir was freshly prepared and degassed just prior to use. Sample solutions were injected into the HT-FIA system through the 0.1-mL loop injector or the auto sampler.

2.3. Catalytic degradation of TPPS and Cu-TPPPS in the presence of metal ions

A reaction sample involving TPPS, $NaIO_4$, metal ion, acetate buffer, and sodium dodecyl sulfate (SDS) was prepared. The pH of the acetate buffer solution was controlled with HCl and NaOH solutions. Cu-TPPS, which was prepared by heating the mixture of 20% excess of Cu(II) to TPPS for 5 min at 100 °C, was occasionally used instead of TPPS. The reaction sample was allowed to stand at room temperature or at 95 °C. The UV–vis spectrum of the sample was measured by the conventional spectrophotometer. Besides, for the HT-FIA analysis, 100 μL aliquot of a freshly prepared sample was injected to HT-FIA.

2.4. Recommended procedure for the determination of Ir(IV)

A 4 mL aliquot of sample solution containing less than 200 pmol of Ir(IV) is placed in a 5 mL volumetric flask, and 0.25 mL of 4×10^{-5} M Cu-TPPS, 0.25 mL of 0.2 M acetate buffer (pH 4–5), and 0.25 mL of 0.02 M $NaIO_4$ are added and diluted to volume with distilled water to 5 mL. Cu-TPPS is prepared in advance from 6×10^{-4} M to 5×10^{-4} M TPPS by heating in 0.01 M acetate buffer (pH 4) for 5 min at 100 °C and then to it was added SDS. The final concentration of SDS is 1%. A 0.1 mL aliquot mixture is injected to HT-FIA system at a constant temperature between 100 and 150 °C and the absorbance change is monitored at 413 nm. The absorbance is measured for the control without Ir(IV) and the concentration of Ir(IV) is determined from the calibration curve, which is made from the absorbance change between control and standard samples.

3. Results and discussion

3.1. Setup of the HT-FIA system

HT-FIA was successfully set up as shown in Fig. 1. Although PEEK tubing instead of stainless tubing was used in the present system for the high temperature reactor tubing to avoid a potential influence of metal ions from the stainless steel tubing, another tubing can be applied for the system. The upper limit temperature of PEEK tubing is normally 250 °C so that we have examined the physical stability of PEEK tubing against high temperature and pressure. Conclusively, the PEEK tubing was stable at temperatures up to 250 °C and at pressures up to 10 MPa. The handling of PEEK tubing is convenience for the exchange or setup of the high temperature reactor. The baseline using an aqueous solution was substantially stable at high temperatures. This is probably due to the fact that the pressure regulator is settled of the upstream of the UV–vis detector so that the solvent through the pressure regulator possesses a fewer pulsating current with notable pressure changes and no influence of evacuations of gases dissolved in the aqueous solutions.

3.2. Degradation behavior of TPPS in the presence of platinum group metal ions

The catalytic activity was discovered by the screening of the combination of metal ions and oxidizing agents in our previous study [11,12]. Ir(IV) exhibited a strong catalytic activity and Rh(III) showed a relatively weak activity for the degradation of TPPS with $NaIO_4$. To confirm this phenomenon, the degradation of TPPS was monitored in the presence of platinum group metal ions at 95 °C. First, we attempted to use TPPS as an indicator reagent for Ir(IV)

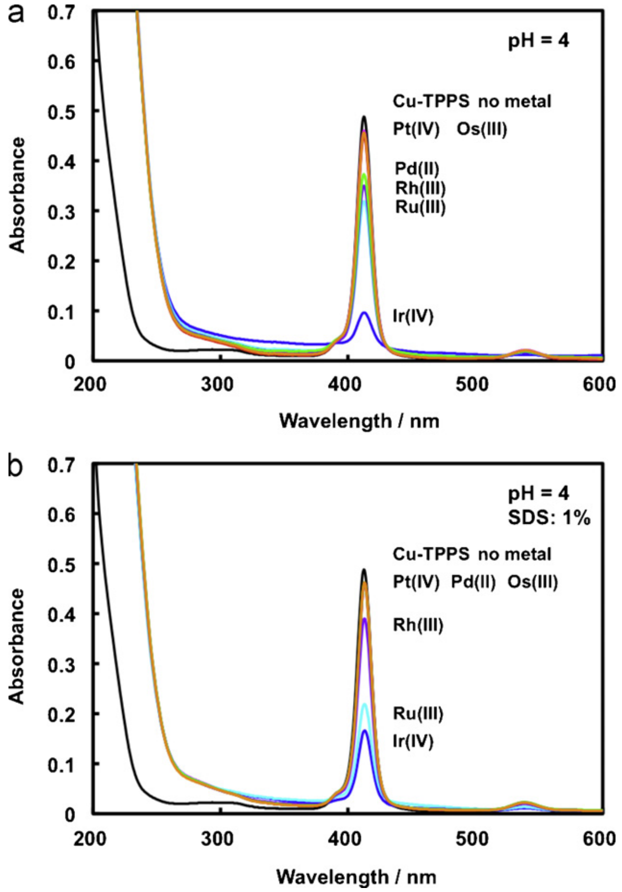

Fig. 2. Absorption spectra for the degradation of TPPS and Cu-TPPS with $NaIO_4$ in the presence of platinum group metal ions. (a) [Cu-TPPS] = 1.0×10^{-6} M, [metal ion] = 1.0×10^{-8} M, [$NaIO_4$] = 1.0×10^{-4} M, [acetate buffer] = 0.01 M, pH 4.0, 95 °C. (b) [Cu-TPPS] = 1.0×10^{-6} M, [metal ion] = 1.0×10^{-8} M, [$NaIO_4$] = 1.0×10^{-4} M, SDS: 1%, [acetate buffer] = 0.01 M, pH 4.0, 95 °C.

catalysis. Absorption spectral changes are shown in supplementary data. The Soret band at 410–440 nm completely disappeared in the presence of Ir(IV) at pH 2–6. The catalytic activity of Ir(IV) was highest at around pH 4–5 (Fig. S1 (a–d) in supplementary data). However, the absorbance change suggests that TPPS is not suitable to use as an indicator reagent for the determination of Ir(IV) ions due to the spectral change of the Soret band at pH 4–5. Thus, we have chosen Cu-TPPS as an indicator reagent instead of TPPS due to the following reasons. First, Cu-TPPS is readily prepared, is stable, and possesses a highest molar absorption coefficient [13]. Second, our previous study showed that Cu-TPPS can be used as an indicator reagent for the determination of Ru(III) [11].

For the degradation of Cu-TPPS, Ir(IV) ion showed the similar catalytic behavior at pH 4 to that using TPPS (Fig. 2a) among the platinum group metal ions while Ru(III), Rh(III), and Pd(II) also showed weak catalytic activities for the Cu-TPPS degradation. It was confirmed that Cu-TPPS is obviously suitable as an indicator reagent for the determination of Ir(IV) as comparing to TPPS. The degradation of Cu-TPPS seems to be somewhat slower than that of TPPS. This would reflect that the kinetic stability of Cu-TPPS for the oxidative degradation would be higher than that of TPPS. The Soret band disappeared and the absorbance at 200–300 nm increased, which indicate that Cu-TPPS was decomposed and unknown degradation products were formed with $NaIO_4$ in the presence of platinum group metal ions. To search optimum conditions the catalytic activity of Ir(IV) was initially examined in the presence of 10^{-4} M $NaIO_4$ at pH 4.0 using HT-FIA.

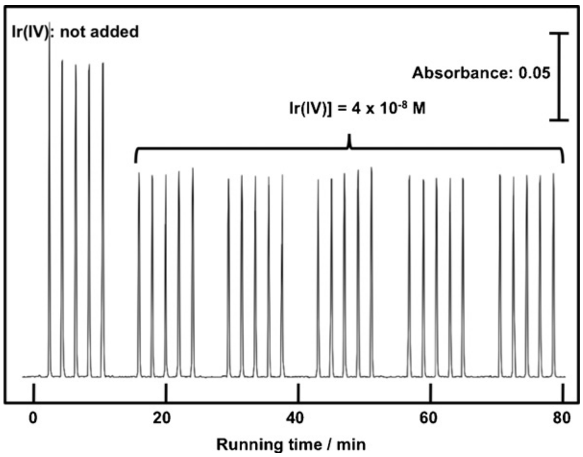

Fig. 3. HT-FIA chart for the detection of the catalytic activity of Ir(IV). [Cu-TPPS] = 1.0×10^{-6} M, [Ir(IV)] = 4.0×10^{-8} M, [$NaIO_4$] = 1.0×10^{-3} M, SDS: 1%, [acetate buffer] = 0.01 M, pH 4.0, 100 °C.

3.3. Influence of SDS for detection for catalytic activity of Ir(IV) using HT-FIA

The reaction mixtures containing Cu-TPPS, $NaIO_4$, acetate buffer and Ir(IV) were injection to HT-FIA system at different flow rates at temperatures. On the course of these investigations, it was found that Cu-TPPS adsorbs on the HT-FIA lines during the detection of Ir(IV) activities and this resulted in a serious tailing of Cu-TPPS. We have inspected to identify the parts, at which Cu-TPPS strongly adsorbs. Conclusively, Cu-TPPS adsorbs the PEEK tubing in the high temperature reactor, the stainless steel tubing, and teflon tubing used connecting HT-FIA constituents since the removal of each part reduced the tailing of Cu-TPPS. It was surprising that the adsorption of Cu-TPPS takes place even at very high temperatures, which would indicate that the strong interactions indeed act between PEEK and Cu-TPPS [14]. Thus, desorption of adsorbed Cu-TPPS was attempted by injection of NaOH solutions since the hydrophilicity of TPPS and its metal chelate decreases due to the protonation at the sulfonates at low pH, which is likely to adsorb on the tubing wall. Naturally, this is not convenient for the observation of catalytic activity of Ir(IV), where a small amount of Cu-TPPS was still eluted even after 7 times washing. The adsorption of Cu-TPPS is interesting since the adsorption of TPPS was not notably observed in our previous study [14–16]. Thus, the strong adsorption of Cu-TPPS would be due to the characteristics of the tubing material and Cu-TPPS. Finally, we concluded that this problem could not be solved by simply reducing the length of tubing or changing the tubing materials. Thus, we have attempted the desorption of Cu-TPPS using surfactants, that is, SDS, Triton X-100, and Brij 35. We found that the addition of 1% SDS significantly improves the problem of Cu-TPPS adsorption on HT-FIA lines, where the concentration is higher than the critical micelle concentration (cmc). It was also confirmed that SDS possesses the strong capability to reduce adsorption of Cu-TPPS as comparing to Triton X-100 and Brij 35. The actual FIA chart support that the tailing is not observed in the presence of SDS (Fig. 3). Furthermore, this result indicates that more than 30 samples can be analyzed within 80 min, which is considered as a high-throughput method.

The catalytic activity of Ir(IV) was indeed investigated in the presence of SDS at 95 °C in batch reactions (Fig. 2b). It was interesting that Ir(IV) possesses a catalytic activity for the oxidative degradation of Cu-TPPS with $NaIO_4$, where SDS micelle should be formed since the concentration of SDS is much higher than cmc. Presumably, Cu-TPPS, IO_4^-, and $Ir(IV)Cl_6^{2-}$ possess negative charges so that these would not interact strongly on the negatively

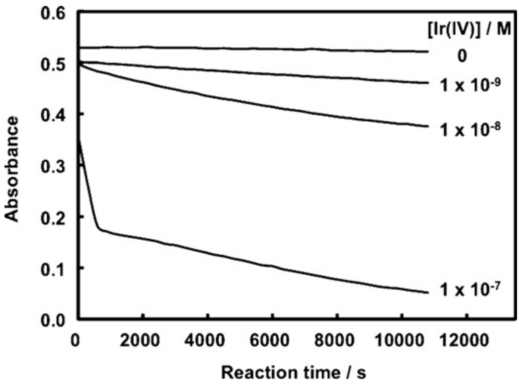

Fig. 4. Disappearance of the Soret band of Cu-TPPS by the oxidative degradation in the presence of Ir(IV). [Cu-TPPS] = 1.0×10^{-6} M, [Ir(IV)] = 0–1.0×10^{-7} M, [$NaIO_4$] = 1.0×10^{-4} M, SDS: 1%, [acetate buffer] = 0.01 M, pH 4.0, 25 °C.

charged SDS micelles. Thus, SDS acts simply for the desorption of Cu-TPPS from the HT-FIA tubing.

3.4. Reaction behavior of the degradation of Cu-TPPS

The reaction curves of the degradation of Cu-TPPS were measured with different concentrations of Ir(IV) (Fig. 4). The reaction curves did not show simple exponential curves and seem to involve two different processes at the Ir(IV) concentration range of 10^{-8}–10^{-7} M. This was also observed in the absence of SDS. The pseudo-first order rate plots of the reaction curve support that these reactions consist of two different reaction processes. In addition, both the reaction rate constants of the rapid part and the slow part were roughly proportional to the concentration of Ir(IV). According to our previous study, the degradation of TPPS and metal–TPPS complexes obeys the pseudo-first-order kinetics. Thus, the present phenomenon simply reflects the unique nature of the oxidation of Cu-TPPS with Ir(IV) and $NaIO_4$. Further analysis of the reaction mechanism would be important as future investigations of the mechanism of Ir(IV) catalyst. Naturally, the fact that the two different pathways are concerned in the present system could be disadvantageous to the determination method of Ir(IV). As mentioned below, controlling the temperatures of the reactor of HT-FIA reduced this problem.

Besides, the pH dependence as shown above suggests that Ir(IV) possess the highest activity at pH 4–5 for TPPS degradation without SDS. This resembles the case of the degradation of TPPS in the presence of Ru(III) and $KBrO_3$.

3.5. Optimization conditions for the determination of Ir(IV) using HT-FIA

3.5.1. $NaIO_4$ concentration

Influence of the concentration of $NaIO_4$ was investigated using 10^{-4}, 10^{-3}, and 10^{-2} M $NaIO_4$ (Fig. 5a). It was observed that the absorbance of Cu-TPPS decreased with increasing of Ir(IV) using the HT-FIA analysis in the presence of 10^{-3} M $NaIO_4$. However, the dependence of absorbance for Cu-TPPS on Ir(IV) was not clearly observed at 10^{-2} M and 10^{-4} M $NaIO_4$. At 10^{-2} M $NaIO_4$ Cu-TPPS decomposed immediately even in the absence of Ir(IV). Besides, the dependence of Cu-TPPS degradation on Ir(IV) concentration is not clear at 10^{-4} M $NaIO_4$.

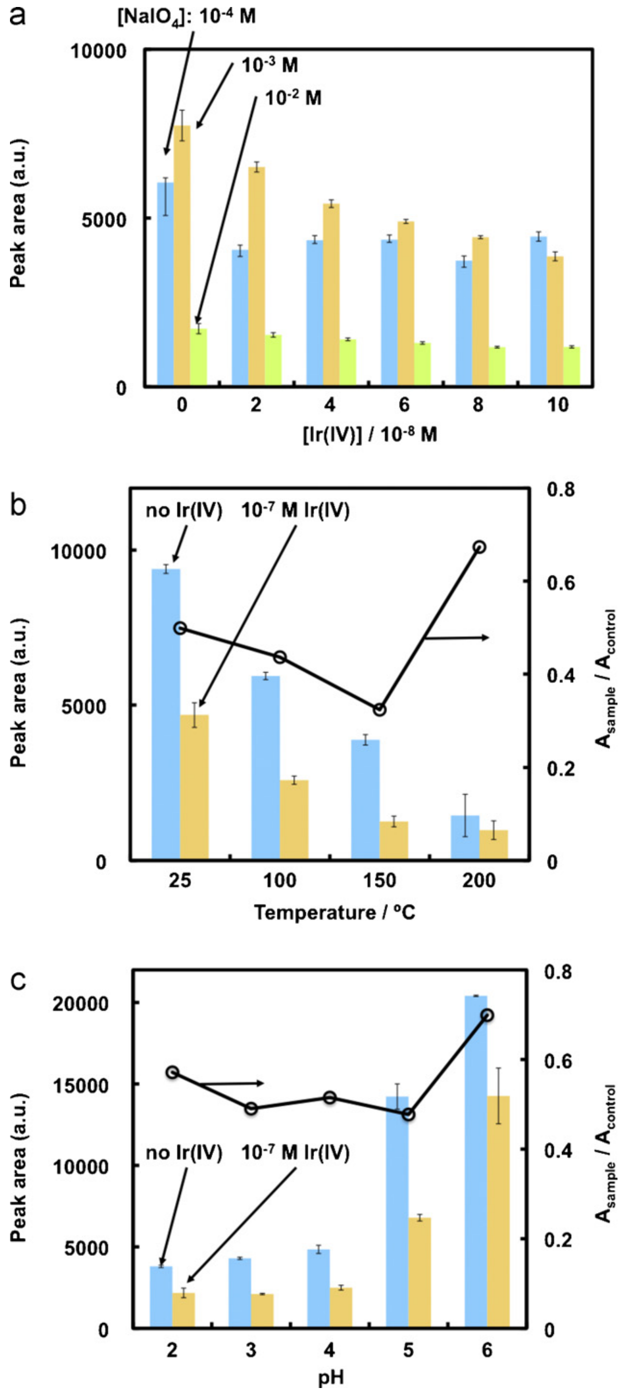

Fig. 5. Influence of $NaIO_4$ concentration, temperature, and pH for the determination of Ir(IV) by using the Cu-TPPS degradation with $NaIO_4$. (a) Influence of $NaIO_4$ concentration. [Cu-TPPS] = 1.0×10^{-6} M, [Ir(IV)] = 1.0×10^{-7} M, [$NaIO_4$] = 1.0×10^{-4}–1.0×10^{-2} M, SDS: 1%, [acetate buffer] = 0.01 M, pH 4.0, 100 °C. (b) Influence of temperature. [Cu-TPPS] = 1.0×10^{-6} M, [Ir(IV)] = 1.0×10^{-7} M, [$NaIO_4$] = 1.0×10^{-3}, SDS: 1%, [acetate buffer] = 0.01 M, pH 4.0. Temperature: 25–200 °C. $A_{sample}/A_{control}$ indicates the ratio between absorbance with Ir(IV) and that without Ir(IV). (c) Influence of pH. [Cu-TPPS] = 1.0×10^{-6} M, [Ir(IV)] = 1.0×10^{-7} M, [$NaIO_4$] = 1.0×10^{-3}, SDS: 1%, [acetate buffer] = 0.01 M, 100 °C, pH 2.0–6.0. $A_{sample}/A_{control}$ indicates the ratio between absorbance with Ir(IV) and that without Ir(IV).

3.5.2. Temperature and pH

The pH dependence as shown above suggests that Ir(IV) possess the highest activity at pH 4–5 for TPPS degradation without SDS. This resembles the case of the degradation of TPPS in the presence of Ru(III) and $KBrO_3$. Here, the degradation of Cu-TPPS with 10^{-3} M $NaIO_4$ in the presence of 10^{-7} M Ir(IV) was investigated at different temperatures and pH (Fig. 5b and c). Both the absorbance without and with Ir(IV) decreased with increasing temperature. However, the ratio between the absorbance with and that without Ir(IV) ($A_{sample}/A_{control}$) showed a minimum at 150 °C. This

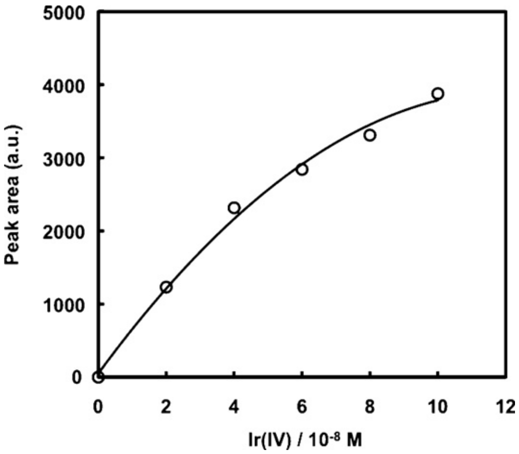

Fig. 6. Calibration graph for the determination of Ir(IV). [Cu-TPPS] = 1.0×10^{-6} M, [$NaIO_4$] = 1.0×10^{-3} M, SDS: 1%, [acetate buffer] = 0.01 M, pH 4.0, 100 °C.

fact indicates that 150 °C is a suitable temperature condition. However, the reproducibility at 100 °C, which is shown as error bars in Fig. 5b, was somewhat better than that at 150 °C. Furthermore, it was observed that the peak area gradually decreased at 25 °C when the same sample was repeatedly injected, the peak area shows a fairly good reproducibility. This is probably due to the following reason. As mentioned above, the degradation of Cu-TPPS involves two processes, where the rapid process of Cu-TPPS degradation proceeds even at low temperatures. Thus, the sample preparation time before the injection of the sample affects the extent of the reaction. However, the fast process entirely proceeds at high temperatures so that the slow process in the presence of Ir(IV) reflects the disappearance of Cu-TPPS peaks on HT-FIA chart (Fig. 6).

Furthermore, it was confirmed that the determination of 10^{-8} M level Ir(IV) was possible using HT-FIA at 250 °C, where the reproducibility was better than that at 25 °C. For this case, the concentration of $NaIO_4$ was reduced to 10^{-4} M (Supporting data Fig. S2(a and b)). Although the disappearance of Cu-TPPS at 250 °C shows better reproducibility, the determination of Ir(IV) seems to be somewhat difficult for 10^{-8} M level Ir(IV). This is due to the dependence of peak height on the Ir(IV) concentration at 10^{-8} M level in the presence of 10^{-4} M $NaIO_4$ at 250 °C is reduced as comparing to that in the presence of 10^{-3} M $NaIO_4$ at 100 °C. This resulted in the difficulty to make a calibration curve at the 10^{-8} M level of Ir(IV) at 250 °C (Fig. S2(b) in supplementary data).

Besides, the degradation behaviors of Cu-TPPS were investigated at pH 2–6 using HT-FIA. The result showed that the magnitude of $A_{\text{sample}}/A_{\text{control}}$ remains fairly constant at pH 3–5 although both the magnitudes of the absorbance with and without Ir(IV) increase with increasing pH. This reflects that both the decomposition rates of Cu-TPPS with and without Ir(IV) decrease with increasing pH at 2–5. At pH 6, the catalytic activity decreases as comparing to pH 5 and lower. These results suggest that an optimum pH condition is between 4 and 5.

3.5.3. *Calibration curve, reproducibility, influences of foreign platinum group metal ions*

The calibration curve was investigated at 10^{-8} M level of Ir(IV). Although the straight line was obtained at 0–4 × 10^{-8} M, the line gradually deviated to lower values from the line. The reproducibility for 5 measurements of 4 × 10^{-8} M Ir(III) was 2.1%. The detection limit of Ir(IV) was calculated to be 5.8 × 10^{-9} M (1.1 ng/mL) based on the reproducibility of the measurement of FIA peaks. The detection limit is fairly low as comparing to previous catalytic determination methods for iridium [17,18].

The influences of other platinum group metal ions for the determination of 4 × 10^{-8} M Ir(IV) was examined. Although 10 times Os(III) did not interfere with the determination of Ir(IV) other platinum group metal ions did interfere with the determination of Ir(IV). Thus, pretreatment and separation would be important for the practice analysis of Ir(IV).

4. Conclusions

A new type of FIA system attached with hydrothermal reactor (HT-FIA) was successfully constructed for the first time and our discovery of the catalytic activity of Ir(IV) for the oxidative degradation of Cu-TPPS with $NaIO_4$ was applied as an indicator reaction for kinetic determination of Ir(IV). HT-FIA enables to readily maintain the high temperature reaction of the kinetic determination of Ir(IV). In addition, the strong adsorption of Cu-TPPS on tubing of HT-FIA was successfully diminished with the addition of SDS in the sample solutions. The detection limit of Ir(IV) reached to 2.5 × 10^{-9} M level. By acceleration of the reaction, a fairly high-throughput analysis, of which more than 30 samples can be analyzed within 80 min by using HT-FIA, was attained. HT-FIA systems would involve potential advantages regarding the notably acceleration of the analytical reactions and the enhancement of selectivity. Thus, further applications of HT-FIA to traditional analytical methods, which have not yet been adapted to FIA because of slow reaction rates, are currently investigated.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.02.038.

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