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High-throughput Ru(III) analysis using the hydrothermal flow reactor-mediated FIA by the extreme acceleration of Ru(III) complexation with 1,10-phenanthroline

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ABSTRACT

A new type of flow injection analysis (FIA) combined with a high-temperature reactor maintained at 100–400 °C, namely hydrothermal flow injection analysis (HT-FIA), has been successfully applied to high throughput determination of Ru(III) on the basis of a conventional chromogenic reaction with 1,10-phenothroline (phen). Although this classical chromogenic reaction using phen is sensitive and selective for Ru(III), the complex formation of Ru(phen)$_3$ requires 2 h. The acceleration using HT-FIA is extraordinary high so that the determination reaction of Ru(III) was successfully shortened to 5 s at 150 °C, where the analytical procedure was accelerated more than 1000-fold. This enabled a high-throughput analysis of Ru(III) with 100 μL sample, of which at least 10 samples can be analyzed within 10 min. The detection limit of Ru(III) determined on the basis of 3 times of standard deviation was 5.3×10^{-7} M (53 pmol or 5.4 ng Ru in 100 μL sample). The present study emphasizes the importance of the revival of classical chromogenic reactions, which are potentially valuable but not regarded anymore as useful because they are time-consuming and tedious, to fit for the demand for environmentally harmless analytical techniques.

1. Introduction

Recent analytical instrumentations, such as ICP-MS, have desperately improved the circumstances of metal analyses so that these devices would be considered to be best fit for practical analytical applications in both fundamental and practical areas [1–3]. However, such methods are not always universal for all types of analytical applications. In addition, the cost of such instruments and the running cost are normally very high so that these instruments are merely useful in limited fields. Demands of high throughput and small sample scale analysis with a low-cost and relatively simple instrument are still widely found in several areas of analytical applications.

Chromogenic reagents and their applications for metal analyses had been extensively investigated in the 20th century [4,5]. However, some of these methods and such classic reagents are not credited now as practical and useful since the analytical procedures are sometime tedious, time-consuming, and require relatively large-scale samples. In other words, several valuable reagents are not anymore focused as useful analytical materials. However, the advantages of the classic reagents should be reminded. The safety for organisms and environment, and characteristics of these materials are well known as compared to newly developed reagents. Large investment to develop new reagents should not be ignored from the viewpoint of environmentally harmless scientific activity.

On the other hand, from the viewpoint of cost and influence to the environment, by developing and maintaining new analytical instruments, relatively classical instruments should be refocused as well as classical analytical reagents. For instance, flow injection analysis (FIA) might be considered to be somewhat a low technology as compared to miniature analytical instruments, such as on-chip devices and μTAS. However, the benefits of FIA [6,7] should be recurrently acknowledged to develop sensitive and reproducible analytical methods by a couple of reasons [8]. First, the technological background of FIA is robust since the fundamental and practical researches have been adequately carried out for many years. Second, FIA systems can be promptly constructed for different purposes as low cost instrumentation and the environmental harmless technology, which are available only in developed countries. Third, FIA still possesses advantages regarding small sample size (practical sample size), high throughput, and capability of automation without miniaturization. Fourth, a variety of modifications are readily applied with attachment of several analytical devices.

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Recently, we have demonstrated the importance and usefulness of the FIA system combined with a hydrothermal flow reactor, namely hydrothermal flow injection analysis (HT-FIA) [9], which was developed on the basis of our hydrothermal flow reactor technology [10–12], which resulted in discovery of new reactions [13,14]. HT-FIA performs extremely high temperature reactions at 100–400 °C within a very short time scale (0.002–200 s) [10]. Although there are several reaction acceleration techniques, such as addition of accelerators for complex formation [15], the acceleration by heating is simplest and most effective unless side reactions do not inhibit the main chromogenic reaction. In addition, heating mechanism by HT-FIA is much simpler than that of microwave heating. By heating, a reaction is accelerated more than 10^8 times by increasing the temperature from 25 °C to 300 °C than the acceleration of the reaction 2 times by increasing temperature with a 10 °C step. In general, the highest temperature using conventional FIA was limited to around 100 °C so that the advantages of heating were not well realized. On the contrary, the reaction temperature using the HT-FIA system can be readily risen up to 400 °C. High temperature reactions in aqueous solutions sometimes exhibit unique features as compared to low temperature reactions since the physical nature of aqueous solutions, such as the dielectric constant, is exceptionally changed. Thus, this enables to develop several unique reactions under hydrothermal conditions [13,14]. The usefulness of HT-FIA has been demonstrated for the acceleration of the indirect indicator reaction of Ir(IV) using a water-soluble porphyrin, where a trace amount of Ir(IV) ion accelerates the oxidative degradation of water-soluble porphyrin [9].

By using HT-FIA, if a classical chromogenic reaction is desperately accelerated, the analytical reaction would be recurrently adopted as a practical analytical method (Fig. 1). According to our previous study, it should be noted that several analytical reagents are fairly stable at temperatures over 100 °C [12]. This fact indicates that conventional reagents could be potentially useful for analytical applications using HT-FIA.

In the present study, we focus on the chromogenic reaction of 1,10-phenanthroline (phen) for Ru(III), which is well known as a sensitive and selective analytical reaction, but requires ca. 2–4 h for the complex formation of $Ru(phen)_3$ [16]. This is considered not to be suitable for the demand for rapid easy procedure and for reduction of sample volume. In addition, the conventional UV–visible technique does not result in high reproducibility and sensitivity as compared to flow analysis. In the present study, we first inspected whether the slow chromogenic reaction of Ru(III) with phen can be actually accelerated using HT-FIA. Second, several analytical conditions, such as reaction temperature, flow rate of HT-FIA, and the amount of reducing agents, were investigated.

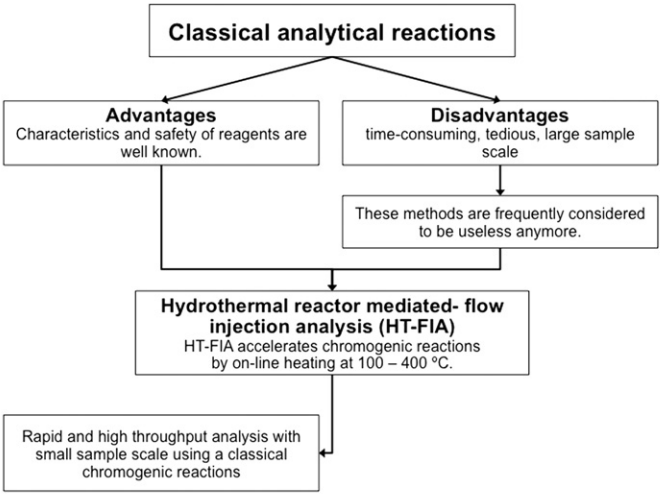

Fig. 1. Principle for the strategy to remake a classical chromogenic reaction suitable for rapid and small sample scale analysis.

2. Experimental

2.1. Reagents and apparatus

1,10-Phenanthroline (phen) was purchased from Wako Pure Chemical Industries Ltd., Japan. Standard solutions for 1000 ppm of Ru(III), Os(III), and Ir(IV) were obtained from Mitsuwa Chemical Co. Ltd., Japan and those of Pt(IV), Pd(II), and Rh(III) were obtained from Wako Pure Chemical Industries Ltd., Japan. Bis(2-hydroxyethyl)iminotris(hydroxymethyl)methane (Bis-Tris) was obtained from Dojindo, Japan. All other reagents used were purchased from Wako Pure Chemical 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. High temperature–pressure resistant vessel (inner volume: 25 mL, Sanai Kagaku Co., Japan) was used for the complex formation reaction of $Ru(phen)_3$ at high temperature.

2.2. Hydrothermal flow reactor mediated-FIA

The set up of a HT-FIA system was based on the previous study [9] (Fig. 2). The system consisted of a solvent reservoir, a high-pressure pump (LC-10AD, Shimadzu Corporation, Japan), a high-temperature reactor, a 100 μL loop injector, 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 (ADL-2020, LCScience, Japan). The UV–Vis detector was attached at the downstream of the pressure regulator. The high-temperature reactor consists of heating blocks and PEEK tubing (inner diameter: 0.25 mm, effective length: 170 cm), which was possible to use at temperatures up to 250 °C within ± 0.2 °C and 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.

2.3. Chromogenic reaction of $Ru(phen)_3$ using a conventional UV–Vis spectrophotometer and HT-FIA

A reaction sample containing Ru(III), phen, $NH_2OH \cdot HCl$, and Bis-Tris buffer (pH = 6.0) was prepared at room temperature. The pH of the Bis-Tris buffer solution was controlled with HCl and NaOH solutions. A 10–15 mL aliquot mixture was incubated in a high pressure–temperature resistant vessel at 100 °C for 2 h. The UV–Vis absorption spectrum at 200–600 nm of the sample was measured by the conventional spectrophotometer. On the other hand, for the HT-FIA analysis a 0.1 mL aliquot mixture was injected to HT-FIA system at a constant temperature between room temperature and -180 °C at a flow rate 1.0 mL min^{-1} and the absorbance at 448 nm was monitored.

2.4. Recommended procedure for the determination of Ru(III)

A 100 μL aliquot of sample solution containing 0.1–4 nmol of Ru(III) is placed in a 500 μL plastic vial, and 0.02 mL of 1×10^{-3} M phen, 20 μL of 3.6×10^{-2} M $NH_2OH \cdot HCl$, 20 μL of 0.1 M Bis-Tris buffer (pH 6), and 40 μL distilled water are added. A 100 μL

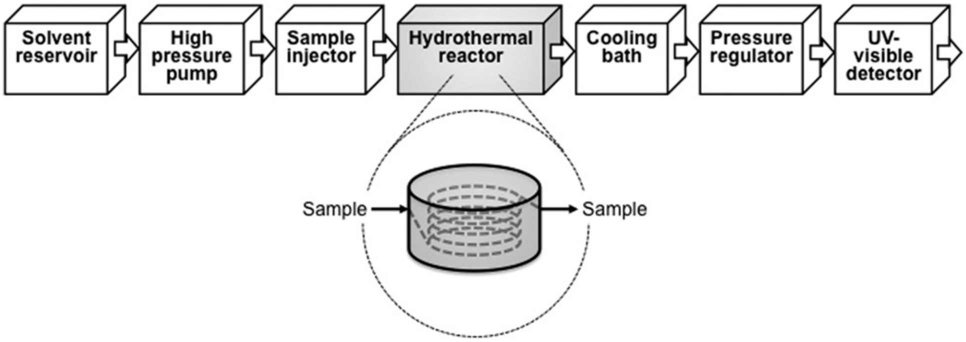

Fig. 2. Set up for flow injection analytical system combined with a hydrothermal reactor.

aliquot mixture is injected to the HT-FIA system at 150 °C at a flow rate 1.0 mL min^{-1}. The absorbance at 448 nm is monitored and the concentration of Ru(III) is determined from the calibration curve.

3. Results and discussion

3.1. Formation of Ru(phen)$_3$ using a conventional technique

The chromogenic reaction for Ru(III) is sensitive and selective among the platinum group metal ions [16]. Ruthenium ion forms charge transfer complex with phen similarly, of which Ru(III) is reduced to Ru(II) in Ru(phen)$_3$ complexes, so that this reaction is potentially selective within platinum group metal ions. The demand of analytical methods for the sensitive and convenient determination of platinum metals have been risen in several fields, such as, the evaluation of platinum group metals evacuated from automobile catalyst [17,18] so that we are recently focusing to develop environmental friendly and rapid analytical method for these metal ions [9,19–21]. However the complex formation of Ru(phen)$_3$ is very slow; generally the complex formation requires ca. 2–4 h heating at 100 °C [16]. The high temperature treatment potentially results in a low reproducibility of determination. In general, the complex formation of platinum group metal ions is slow as compared to the first raw transition metal ions so that the acceleration methods for complexation of platinum group metal ions with chromogenic reagents were frequently developed [19,22,23].

The complex formation of Ru(phen)$_3$ was attempted in the presence of reducing agent NH_2OH. Fig. 3 shows the molar ratio plots for Ru(phen)$_3$ complex, which were prepared by incubation at pH 6 at 100 °C for 2 h in a high temperature resistant vessel on the basis of previous method [16]. The amount of NH_2OH is sufficient to reduce Ru(III) to Ru(II) to form the stable charge transfer complex with phen. The complex formation behaves similarly to the case of complex formation Fe(III) in the presence of NH_2OH. The spectrum possesses a maximum absorption band at 448 nm, which is somewhat different from that of Fe(phen)$_3$ complex. Significant difference between the formation of Ru(phen)$_3$ and Fe(phen)$_3$ is the fact that the reaction rate of Ru(III) with phen is much slower than Fe(III). The reaction rate is shown in Fig. 4, which indicates the relationship between the absorbance at 448 nm as a function of reaction time. This fact indicates that the reaction requires 2–4 h. Along these lines, it is realized that the analytical procedure is not sometimes practical.

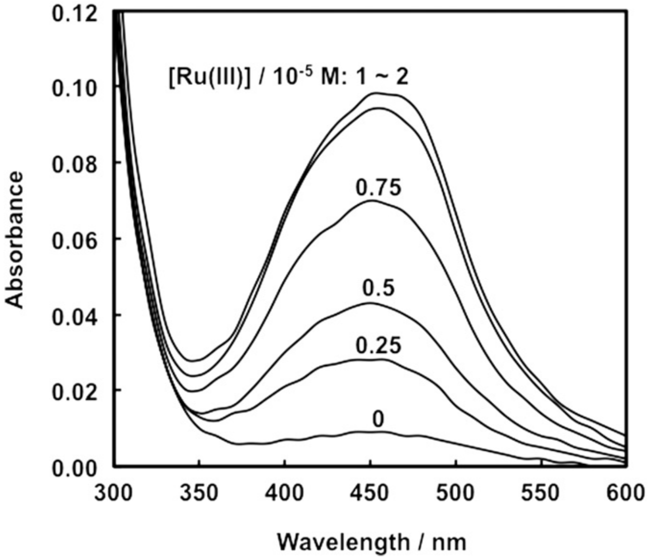

Fig. 3. Formation of Ru(phen)$_3$ complex as a function of Ru(III) concentration. [Ru(III)]$=0\sim2\times10^{-5}$ M, [phen]$=3\times10^{-5}$ M, [NH_2OH]$=3.6\times10^{-3}$ M, [Bis-Tris]$=10^{-2}$ M (pH 6.0), 100 °C, 2 h. Absorption spectra were determined using a conventional spectrophotometer.

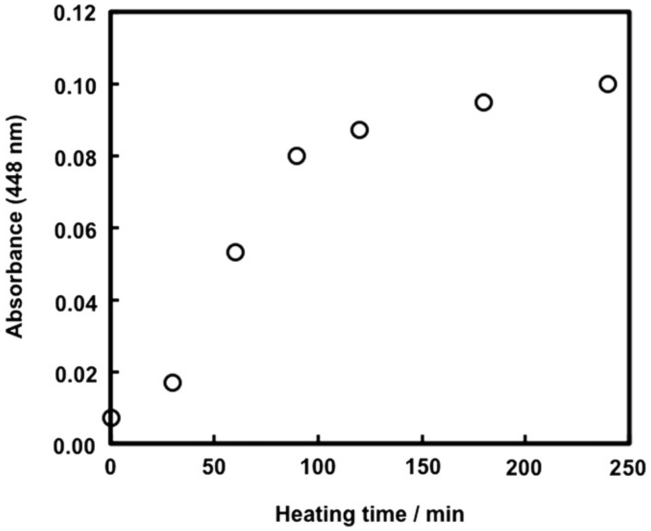

Fig. 4. Heating time for complex formation of Ru(phen)$_3$. [Ru(III)]$=1.0\times10^{-5}$ M, [phen]$=3\times10^{-5}$ M, [NH_2OH]$=3.6\times10^{-3}$ M, [Bis-Tris]$=10^{-2}$ M (pH 6.0), 100 °C.

3.2. Formation of Ru(phen)$_3$ using HT-FIA

Based on the previous study for the complex formation of Ru(III) with phen, the concentration range of Ru(III) and phen, pH, and the usage of reducing agent NH_2OH were applied for the online chromogenic reaction of Ru(III) with phen using HT-FIA. However, there would be unknown factors for a direct application

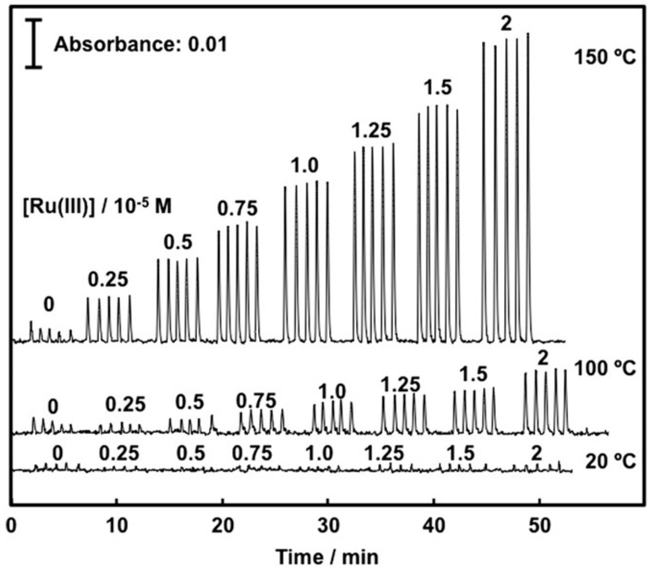

Fig. 5. Charts for HT-FIA measurement of ruthenium. [Ru(III)] = 0–2.0 × 10^{-5} M, [phen] = 1.0 × 10^{-4} M, [NH_2OH] = 3.6 × 10^{-3} M, [Bis-Tris] = 10^{-2} M (pH 6.0), injection volume: 100 μL, 448 nm, flow rate: 1 mL/min. Temperature: 20, 100, 150 °C.

of these conditions from the conventional spectrophotometric technique to the flow technique. For instance, our first demonstration with a water-soluble porphyrin as an indicating reagent for iridium using HT-FIA, adsorption of the porphyrin onto inner wall of tubing lines was an important issue. This problem was solved using sodium dodecyl sulfate. However, it was not expected that phen did not show any adsorption onto the tubing materials used in HT-FIA. The HT-FIA chart shown in Fig. 5 demonstrates the evolution of peaks for Ru(III), which are due to the complex formation of Ru($phen)_3$ at temperatures 20, 100, and 150 °C. The flow rate was 1.0 mL min^{-1} so the residence time, of which the sample is exposed in the hydrothermal flow reactor, is 5 s. The peak was fairly symmetrical and showed no tailing. However, the evolution of absorbance at 448 nm increases with increasing temperature up to 150 °C and drops at 180 °C (Fig. 6). The increase of the absorbance between 20 and 150 °C is due to the acceleration of complex formation of Ru($phen)_3$. The decrease of absorbance at 150–180 °C is probably due to degradation of Ru($phen)_3$ at high temperature.

The influence of reducing agent NH_2OH was investigated on the peak height of Ru($phen)_3$ as shown in Fig. 7. The results indicate that stoichiometric amount of NH_2OH is not efficient to reduce Ru(III) to Ru(II) in Ru($phen)_3$. This is probably due to that the reduction of Ru(III) is not sufficiently fast within the residence time or NH_2OH is degraded in the HT-FIA system. Thus, more than 100 times larger amount was necessary to reduce Ru(III) to enhance peak height. Addition of 3.6 × 10^{-2} M NH_2OH indicates that Ru($phen)_3$ can be partially destroyed. It is regarded that the degradation of phen and/or Ru($phen)_3$ complexes does not results in problems for analysis of Ru(III).

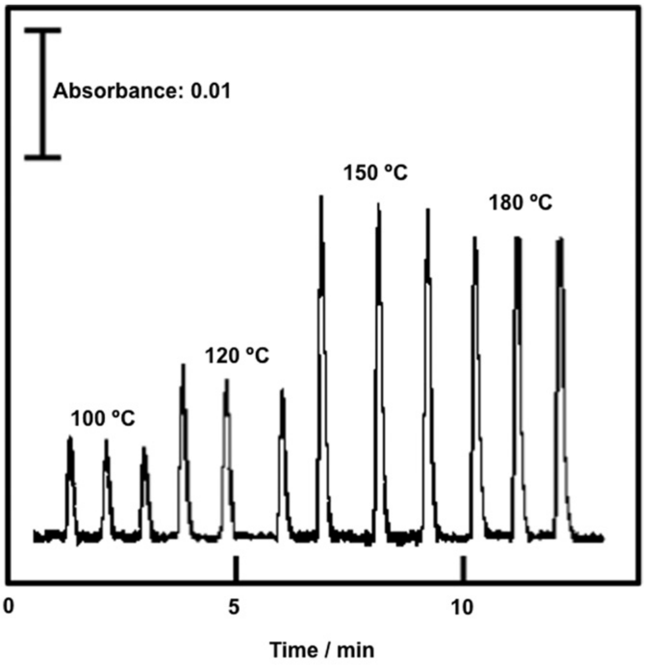

Fig. 6. Influence of temperature for HT-FIA measurement of ruthenium. [Ru(III)] = 1.0 × 10^{-5} M, [phen] = 1.0 × 10^{-4} M, [NH_2OH] = 3.6 × 10^{-3} M, [Bis-Tris] = 10^{-2} M (pH 6.0). Injection volume: 100 μL, detection: 448 nm, flow rate: 1 mL/min.

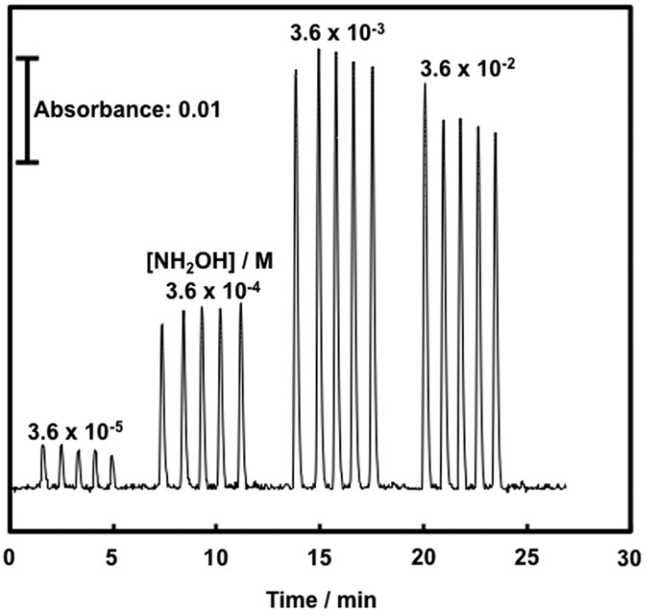

Fig. 7. Influence of NH_2OH concentration for HT-FIA measurement of ruthenium. [Ru(III)] = 1.0 × 10^{-5} M, [phen] = 1.0 × 10^{-4} M, [NH_2OH] = 3.6 × 10^{-5}–3.6 × 10^{-2} M, [Bis-Tris] = 10^{-2} M (pH 6.0), 150 °C. Injection volume: 100 μL, detection: 448 nm, flow rate: 1 mL/min.

3.3. Calibration curve, reproducibility, and interference by foreign platinum group metal ions

The calibration curves at 150 °C for Ru(III) are evaluated. A straight line was obtained with correlative coefficient 0.996. The apparent molar absorptivity at 150 °C was 3.1 × 10^3 cm^{-1} M^{-1} and the standard deviation was 0.9% for 10 times injection of 1 × 10^{-5} M Ru(III). These indicate that the determination of Ru(III) using HT-FIA is sufficiently accurate as a determination method. The calibration curves determined at 100 °C showed much smaller slopes, where the apparent molar absorptivity was 0.92 × 10^3 cm^{-1} M^{-1}, which is 30% at 150 °C. Although the apparent molar absorptivity is not very high as comparing to other chromogenic methods as well as the original Ru(III) chromogenic reaction with phen, the detection limit, which was calculated on the basis of 3 times of the standard deviation, reached to 5.3 × 10^{-7} M. This corresponds to the 53 pmol or 5.4 ng Ru in a 100 μL sample and this fact indicates that the detection limit on the basis of the absolute amount of Ru is fairly low. The determination range of Ru(III) is 0.053–2 μg mL^{-1}.

Table 1
Recovery of Ru(III) in the presence of foreign platinum group metal ions.

	Recovery (%) of 10^{-6} M Ru(III)	
Platinum group metal ions added	10^{-5} M (10-fold)	10^{-4} M (100-fold)
None	100	100%
Rh(III)	102	117
Pd(II)	101	110
Os(IV)	101	190
Ir(IV)	98	110
Pt(IV)	62	60

$[\text{Ru(III)}]=10^{-6}$ M, $[\text{phen}]=10^{-4}$ M, $[\text{NH}_2\text{OH}]=3.6\times10^{-3}$ M, $[\text{Bis-Tris}]=10^{-2}$ M (pH 6.0).

On the other hand, the apparent molar absorptivity for Ru(III) using the conventional UV–Vis spectrophotometer was 8.4×10^3 cm^{-1} M^{-1} with the correlative coefficient 0.989 on the basis of the calibration curve between $0-1.0\times10^{-5}$ M Ru(III). The accuracy for HT-FIA was slightly higher than that using the conventional method is probably due to the fact that the conventional method need a complex formation reaction for 2–4 h using a high temperature and pressure resistant vessel, which potentially results in leaking the sample solution. From this viewpoint, HT-FIA is superior to the conventional technique. Thus, the detection limit using the conventional technique is primarily dependent on the reproducibility of the complex formation of Ru(III) with phen using high temperature and pressure resistant vessel.

Conclusively, although the apparent molar absorptivity is not very high, the present method is fairly sensitive and the detection limit is competitive or somewhat high as compared to other spectrophotometric methods [24], and indirect catalytic determination methods [25,26]. The determination range of Ru(III) in the previous method [24] is 0.25–13.43 μg mL^{-1} so the present method is of lower range for Ru(III). This would be due to the merit of FIA with a small scale of sample. In addition, the sample can be readily prepared by just mixing the reagent and a sample containing Ru(III). Thus, the analytical procedure including sample preparation can be entirely automated. Conclusively, the advantage using HT-FIA due to the extraordinary acceleration of the conventional chromogenic reaction resulted in high throughput analytical tool with fairly good sensitivity.

The influences of other platinum group metal ions for the determination of 1×10^{-5} M Ru(III) were examined as shown in Table 1. Although 10 times Rh(III), Pd(II), Os(IV), and Ir(IV) did not interfere with the determination of Ru(III), Pt(IV) did interfere with the determination of Ru(III). 100 times Rh(III), Pd(II), and Ir(IV) interfered somewhat and Os(IV) interfered strongly the determination of Ru(III) (Table 1). Thus, pretreatment and separation would be important for the practical analysis of Ru(III).

4. Conclusions

High throughput analysis (at least 10 samples per 10 min) of Ru(III) with small sample volume using a classical chromogenic reaction with 1,10-phenanthroline was achieved by hydrothermal flow injection analysis. The detection limit of Ru(III) reached to 5.3×10^{-7} M where the apparent molar absorptivity was 3.1×10^3 cm^{-1} mol^{-1} dm^3. Although the apparent molar absorptivity was reduced to ca. 1/3 as comparing to the original molar absorptivity, the heating time was reduced to 5 s by HT-FIA from 2 h (more than 1000 times) as comparing to the conventional method. The results showed that HT-FIA has a strong potential for acceleration of chromogenic analytical reactions. There are several classical and traditional chromogenic reactions, which possess an advantage, that is, the characteristics and safety of the reagents are well known, but not considered as useful anymore because of their tedious and time-consuming procedure. The present study showed that such classical analytical reactions and reagents are still useful to design rapid, practical, and environment friendly analytical processes.

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