



# Determination of ultra-trace Pt, Pd and Rh in seawater using an off-line pre-concentration method and inductively coupled plasma mass spectrometry

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## HIGHLIGHTS

- An off-line pre-concentration method for Pt, Pd and Rh in seawater was developed.
- The method had low system blanks and could quantitative recovery Pt, Pd and Rh.
- The method is easy to operate and the enrichment factor could reach to 200-fold.
- This method successfully tested the actual samples and obtained excellent results.

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## ABSTRACT

A method was modified for the preconcentration of platinum (Pt), palladium (Pd) and rhodium (Rh) from seawater by a solid phase extraction using a commercially available resin Nobias-chelate PA1<sup>®</sup>. All the determination was conducted using inductively coupled plasma mass spectrometry (ICP-MS) which had a low detection limit for Pt, Pd and Rh, about 16.53, 16.41 and 26.88 pg L<sup>-1</sup>, respectively. It was found that the adsorption performance of the resin was closely related to the matrix, ligands and pH of the samples. Significant difference in recovery was found in various samples: seawater ≈ artificial seawater > ultra-pure deionized water. This method had low method blank in the range of 5.51–8.89 pg L<sup>-1</sup> and high enrichment factor of up to 180–200. The recoveries of Pt and Pd were 93 ± 4.2% in the spiked real seawater. However, the recovery of Rh on the resin was below 70% but stable in the range of 65–68%. It indicated that the Rh recovery seemed to be reproducible and higher volumes of seawater must be processed in order to obtain the lower limit of quantification and excellent recovery.

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## 1. Introduction

Platinum group elements (PGEs; including Pt, Pd, Rh, Os, Ir and Ru) are trace elements with the content less than 1 μg kg<sup>-1</sup> in the crust (Reith et al., 2014). However, these elements are widely used in modern industry because of their excellent characteristics such as antioxidant, catalytic activity, and corrosion resistance

(Wiseman and Zereini, 2009; Pawlak et al., 2014). Hence, an enormous amount of PGEs would be released into the environment with anthropogenic activities, especially the application of automobile catalytic system (Palacios et al., 2000; Ek et al., 2004; Wang et al., 2007; Ruchter and Sures, 2015). Current evidence has demonstrated their potential risks to human health and ecology (Kielhorn et al., 2002; Ravindra et al., 2004; Ducoulombier-Crépineau et al., 2007). For instance, the element Pt could get into the cells through the human skin and block some special biochemical reactions (Gebel et al., 1997; Schmid et al., 2007). Moreover, Pt, Pd and Rh could accumulate significantly in plants, eggs and some biological species (Turner et al., 2007; Bonanno, 2011; Alméjía et al.,

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2016). Furthermore, the solubility of PGEs could be enhanced with the presence of common compounds in the environment and their ions would mobilize and transform easily (Leopold et al., 2008; Reith and Cornelis, 2017). Therefore, it is necessary to monitor PGEs in various environment matrixes to investigate their bioavailability, biogeochemical behavior, and toxicity (Calvo Fornieles et al., 2016). In the past decades, researchers focused on the concentration level of PGEs in urban road dusts, organisms, sediments, and rivers (Turner et al., 2007; Bonanno, 2011; Cobelo-García et al., 2011; Suzuki et al., 2014; Alméjida et al., 2016; Mashio et al., 2016). Nevertheless, the geochemical behavior of these elements has been known little in the marine environment, even in the coastal areas that are widely and profoundly influenced by human activities and river input. The limiting factors are the low concentration of PGEs and the coexisting elements in seawater (Machado et al., 2017) which could interfere in the detection of PGEs by reducing the analytical sensitivity of the instruments.

In response to the low value and complicated environment matrices, voltammetry techniques (Van den Berg and Jacinto, 1988; Cobelo-García et al., 2014) and pre-concentration approaches (Suzuki et al., 2014; Calvo Fornieles et al., 2016; Fischer et al., 2018) have been developed for the determination of PGEs in water samples at ultra-trace concentrations. Among these analytical methods, solid-phase extraction is considered as a preferable pre-concentration procedure because it is reproducible, faster, cleaner, and requires smaller volumes of solvent and sample (Mladenova et al., 2012). Moreover, chelate resin extraction coupled with ICP-MS or ICP-OES has been proven to be a powerful tool for an accurate multi-element analysis over a wide range of concentrations in seawater (Biller and Bruland, 2012; López Guerrero et al., 2016, 2017). For those, many synthesized or commercially available chelate resins have been used to extract PGEs from different matrixes, but a limited number of them are applied in PGEs analyses in seawater (Biller and Bruland, 2012; Hatje et al., 2014; Suzuki et al., 2014; López Guerrero et al., 2016, 2017). Calvo Fornieles et al. (2016) used an anion exchange chelating resin [silica gel functionalized with 1,5-bis (di-2-pyridyl) methylene thiocarbonylhydrazide] to simultaneously separate Pt, Pd and Ir from seawater and on-line determine their concentrations with ICP-OES. The method obtained an excellent recovery of Pt, Pd and Ir, about 94.5–105.8%. Furthermore, Bio-Rad AG<sup>®</sup> 1-X8 as a commercially available anion exchange resin has been used to extract Pt in seawater at ultra-trace concentration (Suzuki et al., 2014; Mashio et al., 2016) but its application in the enrichment of Pd and Rh is limited (Bertine et al., 1996). Fischer et al. (2018) proposed a method for the pre-concentration of Ag and Pt in seawater with the strong anion exchange resin Dowex<sup>®</sup> 1X8 and successfully applied this method to the detection of actual and reference samples. Hence, it is meaningful and promising to test the availability of a chelating resin that is commercially available and could simultaneously extract Pt, Pd and Rh in seawater. Nobias-chelate<sup>®</sup> PA1 seems to have this potential because of its strong affinity with a wide variety of trace metals by two functional groups: ethylenediaminetriacetic acid (EDTriA) and IDA (Sohrin et al., 2008). Moreover, this resin has been applied to the extraction of ultra-trace rare-earth elements from seawater simultaneously and expressed strong matrix tolerance (Persson et al., 2011; Takata et al., 2011; Hatje et al., 2014). Finally, it is a commercially available resin with stable property.

Therefore, an off-line method for simultaneous extraction of Pt, Pd and Rh in seawater by Nobias-chelate PA1<sup>®</sup> resin was proposed in present research. This method was modified and improved based on some former studies (Sohrin et al., 2008; Biller and Bruland, 2012; Lagerström et al., 2013; Hatje et al., 2014). The operation could be simply controlled and less contaminated, and allows for

the loading of multiple samples simultaneously. We applied this method to extract Pt, Pd and Rh that are considered as the main PGEs pollutants in seawater and determine real coastal surface seawater in the North Yellow Sea. Unfortunately, due to the lack of Pt, Pd Rh references in our research, the recoveries of these elements were only conducted in spiked standard reference solutions (natural seawater).

## 2. Experiment

### 2.1. Reagents

The reagents mentioned in this research were trace metal grade (TMG) and supplied by Fisher Scientific. In order to avoid contamination and reduce the reagent blanks, concentrated nitric acid and concentrated hydrochloric acid were subjected by distillation of those TMG reagents in a sub-boiling distillation apparatus (DST-1000, Savillex<sup>™</sup>). The ammonium acetate (NH<sub>4</sub>Ac) buffer solution used to adjust the pH of the sample was produced by acetic acid (HAc) and NH<sub>4</sub>OH. The Nobias-chelate PA1<sup>®</sup> resin used in this research was manufactured by Hitachi High-Technologies with an average particulate diameter of ~60 μm. The low-density polyethylene (LDPE) bottles (Nalgene<sup>™</sup>, Thermo Fisher Scientific Inc.) used for the storage of buffer solutions, seawater samples, standards and elution reagents were prepared following a strict acid cleaning process, and the ultra-pure deionized water (QW) (>18 MΩ-cm) used in this study was produced by a Milli-Q (MQ) system. The reagent bottles were soaked with 10% HCl for ~24 h and then stored in 10% HNO<sub>3</sub> for another 24 h and then washed 3–5 times with QW. The sample bottles (50 mL, BD FALCON<sup>™</sup>) and elution bottles (15 mL, BD FALCON<sup>™</sup>) were cleaned by being filled with 3 M HNO<sub>3</sub> and heated overnight in an ultrasonic cleaner, and then this operation was repeated in 3 M HCl. All the experimental wares were dried in a Class 100 clean bench. The mixed stock solution of 1000 mg L<sup>-1</sup> Rh, Pt and Pd in 2 M HCl was supplied by General Research Institute for Nonferrous Metals. The experimental operations were conducted in the HEPA filtered workbenches (Class 100) in a trace-metal clean laboratory (Class 100, 22–25 °C) in the First Institute of Oceanography, State Oceanic Administration of China.

### 2.2. Instrument and analysis

In this study, the samples were measured using an inductively coupled plasma-mass spectrometer (ICP-MS, Element 2, Thermo Fisher Scientific Inc.) fitted with an Apex HF micro-nebulizer system (Elemental Scientific Inc.), and an internal standard (indium, 1 μg L<sup>-1</sup>) was spiked in every sample. The instrument was optimized by pumping a 1 μg L<sup>-1</sup> tune solution (Li, Ce, Ba, In and U) to monitor the oxide formation (BaO/Ba <3%) and the sensitivity of In (1 μg L<sup>-1</sup>) was about 4,000,000 cps. Considering individual isotopic abundance, the data of the target elements were collected by measuring the most abundance mass of <sup>104</sup>Pt, <sup>105</sup>Pt, <sup>105</sup>Pd, <sup>106</sup>Pd, <sup>108</sup>Pd and <sup>103</sup>Rh in low resolution with a mass resolving power of 300 (m/Δm at 5% peak height). The potential interference on Pt and Rh was assessed based on the data of <sup>178</sup>Hf and <sup>64</sup>Zn (Simitchiev et al., 2008; Fischer et al., 2018). The isobaric interference on Pd was corrected by monitoring <sup>200</sup>Hg and <sup>111</sup>Cd, and the data of <sup>108</sup>Pd and <sup>65</sup>Cu, <sup>68</sup>Zn, <sup>85</sup>Sr, <sup>89</sup>Y and <sup>95</sup>Mo was used to monitor the potential polyatomic interference. As a quality control, a standard solution containing 0.1 μg L<sup>-1</sup> of Pt, Pd and Rh in 1 N HNO<sub>3</sub> was run on the ICP-MS after the analysis of every 12 samples. The instrument blank was estimated by running 1 N HNO<sub>3</sub> acid after a run of per 12 samples during the detection to correct the instrumental baseline drift. The analytical parameters of the method are shown in Table 1.

**Table 1**

Analysis parameter of the extraction method. Detection limit (LOD) and quantification limit (LOQ) are the results of the two individual channels in the extraction system.

	Pt	Pd	Rh
Enrichment factor	180–200	180–200	180–200
LOD (pg L <sup>-1</sup> )	16.5 ± 0.7	16.4 ± 0.4	26.7 ± 0.9
LOQ (pg L <sup>-1</sup> )	55.1 ± 2.3	54.7 ± 1.4	89.6 ± 3.1

### 2.3. Sample collection

Samples used in this study were surface seawater (2–3 m deep) collected on two sampling trips. One trip was in May 2015, and the other one was in March 2016. The sampling stations are shown in Fig. 1. The seawater sample used as the spiked standards was collected from station B23 in the North Yellow Sea in May 2015 and acidified to pH ~2 with concentrated HNO<sub>3</sub>. In March 2016, the samples were collected from 5 stations, namely 3, 9, 15, S7 and S8, which were used for the test on actual samples. The sampling followed a strict trace-metal cleaning procedure that was modified based on Li et al. (2015). The sampling system consisted of a portable peristaltic pump (Cole-Parmer Inc.) equipped with pre-cleaned C-flex<sup>®</sup> tubing (Cole-Parmer Inc.), and the intakes and connections were Teflon material. Seawater samples were filtered in-line through a 0.2 µm capsule Opticap<sup>®</sup> polyethersulfone filter (Millipore Inc.), collected in a pre-cleaned 1 L LDPE bottle (Nalgene<sup>™</sup>, Thermo Fisher Scientific Inc.), and then acidified to a pH ~2 with concentrated HNO<sub>3</sub>. The samples were stored frozen (–20 °C) and approximately 1 mL concentrated HCl was added to each of them before the extraction experiment to transform the complex of PGEs to M(Cl)<sub>n</sub><sup>m-n</sup> (m = 2–5; n = 4–6) (Colombo et al., 2008; Gerber et al., 2010).

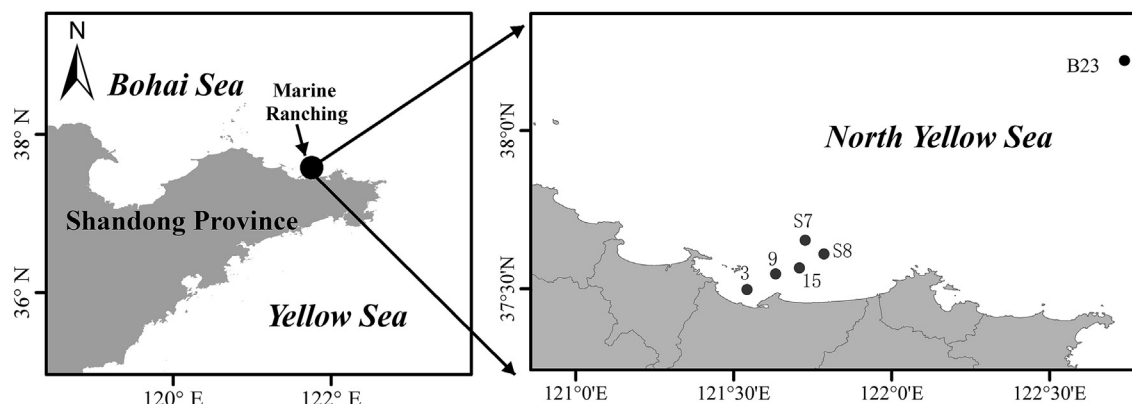
The cleaning procedure was performed according to Li et al. (2015). The C-flex<sup>®</sup> tubes were first washed with Decon90<sup>®</sup> and soaked with 10% HCl for 24 h, and then stored in 2% HNO<sub>3</sub> for further use. The sample bottles were also pre-cleaned using Decon90<sup>®</sup>, but then washed with 30% HNO<sub>3</sub>, 30% HCl and QW respectively, followed the details in Li et al. (2015). Each bottle was double bagged in polyethylene bags, and stored (at 20–25 °C) for further use. The Millipore<sup>®</sup> filters were pre-cleaned with 2% HNO<sub>3</sub> and then rinsed with QW before use.

### 2.4. Pre-concentration process

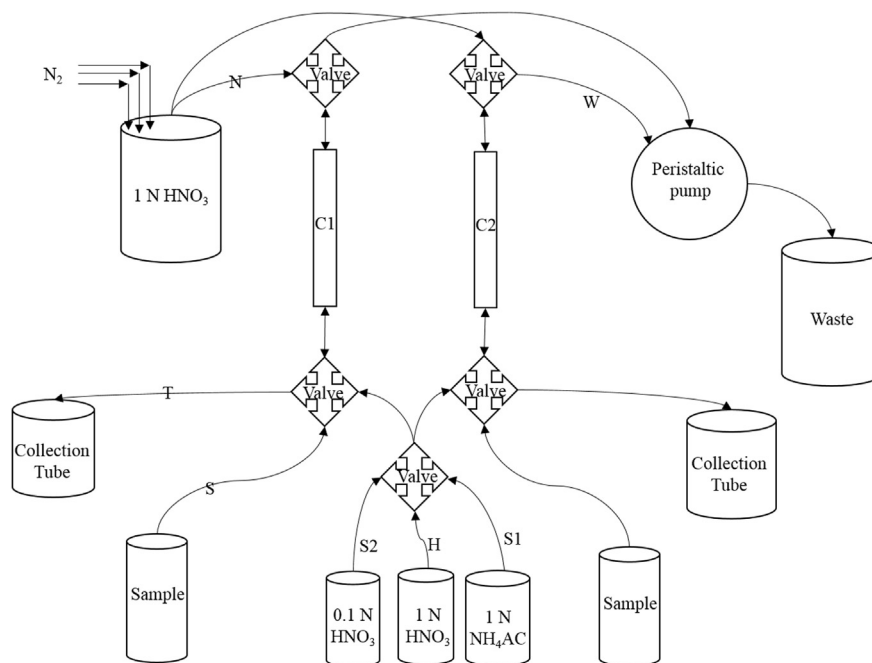
The pre-concentration system used in this study was adjusted and developed based on a reported method (Biller and Bruland,

2012; Hatje et al., 2014). We did not change the specific structure of the extraction system, but only adjusted the volumes of samples and elutions. The schematic diagram of the extraction process is shown in Fig. 2. The extraction system was connected by 1/16" O.D. × 0.04" I.D. perfluoroalkoxy (PFA) Teflon tube (IDEX) and 4-way PEEK flow switching valves (IDEX), which could simultaneously operate 2 samples. A 6-channel peristaltic pump (LongerPump<sup>®</sup>, Longer Precision Pump Co. Ltd) was used to load the samples and rinse the system at a flow rate of about 0.5 mL min<sup>-1</sup>. The elution was operated by pressurizing the system using high purity nitrogen at a pressure of 3–5 psi. The extraction chamber used in the system was a 2 cm long micro column (non-metal frits, Global FIA) with an inner volume approximately 27 µL, and this type of column has been widely used in flow-based devices for preconcentrating metal elements from seawater samples (Biller and Bruland, 2012; Hatje et al., 2014). The Nobias-chelate PA1<sup>®</sup> resin, pre-activated in 1 M HCl, was loaded into the column using a pipette (10–100 µL; Eppendorf Reference<sup>®</sup>).

The enrichment devices, including injection tubes, valves and columns, were pre-cleaned with 10% HNO<sub>3</sub>. It is important to note that the PFA tube wall should be continuously flushed with 10% HNO<sub>3</sub> and QW, and the resin in the column should be soaked in 0.1 N HNO<sub>3</sub> (>24 h). Prior to the loading of the samples, the HNO<sub>3</sub> in the extraction system was emptied and four-way valves were adjusted to connect the H-C1-W line. About 8–10 mL 1 N HNO<sub>3</sub> was loaded to flush the tube and activate the resin. Then, S1-C1-W was connected, and the resin was washed with ~3 mL of 0.05 M NH<sub>4</sub>Ac buffer. This operation was to ensure the resin was suitable to adsorb the Pt, Pd and Rh ions in the sample by changing the exchange sites of the resin from the H<sup>+</sup> to the NH<sub>4</sub><sup>+</sup> form (Hatje et al., 2014). Then, ~200 mL of pre-weighed sample (adjust pH to 7.0 ± 0.2 by 3.7 M of NH<sub>4</sub>Ac with the pH 9.54 ± 0.2) was passed through the extraction unit at the flow rate of 0.5 mL min<sup>-1</sup>. After the loading of the sample, the four-way valve was adjusted to connect the S1-C1-W line, and ~3 mL 0.05 M NH<sub>4</sub>Ac was pumped through the system. In this step, interfering ions, such as Cl and Na<sup>+</sup>, which attached to the resin's surface, were removed. Finally, Pt, Pd and Rh which retained on the resin were eluted with 1 N HNO<sub>3</sub> using the line N-C1-T. The rinsing process was driven by high purity nitrogen at a pressure of 3–5 psi and about 1 mL of elution was collected. After elution, ~3 mL of 1 N HNO<sub>3</sub> was passed through the column for the testing of the effects of the eluent amount on the leaching efficiency and the elimination of the carryover between the samples. The high recycling rate of the Nobias-chelate PA1<sup>®</sup> resin has been demonstrated, and hundreds of samples could be extracted by one column (Biller and Bruland, 2012; Hatje et al., 2014). It was worth noting



**Fig. 1.** Study area and sampling sites in the coastal water of the North Yellow Sea. The black dots in the right panel indicate the sampling sites.



**Fig. 2.** Schematic diagram of the extraction process. The capital letters (B, C, H, N, S, S1, S2 and T) represent the solution route; each valve is a four-way switch that controls the flow of solutions. This system allows for loading 2 samples simultaneously.

that the quality of the collection vials should be weighed before and after elution to obtain the mass of the elution sample. Method blanks including the contribution of the rinse, the elution acid, the PA1 resin and the instrument were produced by loading 200 mL of sample pre-cleaned by PA1 resin five times in each extraction channel (Biller and Bruland, 2012; Hatje et al., 2014; Fischer et al., 2018).

Considering the strong complexation of Pt, Pd and Rh with organic matter (Turner et al., 2008; Cobelo-García, 2013), we investigated the interference of organic matter in seawater on the pre-concentration. The sample was irradiated at 220 V/60 Hz for 200 min (Kuma et al., 1996; Achterberg et al., 2001) in the UVO-Cleaner® irradiated apparatus (Model NO. 5144AX-220, Jelight Inc.). The reaction chamber was a 200 mL PFA tank which was covered with a quartz cover embedded in a lid. The background DOC concentration of the UV digested sample was detected by a total organic carbon analyzer (TOC-V<sub>CPH</sub>, Shimadu) and was less than 0.01 mg L<sup>-1</sup>.

## 2.5. Data calculation and correction

The concentrations of PGEs in the samples were calculated based on the following quantitative equations. The (1) and (2) were the basic formula. Equation (1) is used to calculate the enrichment factor (F): the ratio of sample mass to eluent mass. Consider the breakthrough of the resin, the uncontrollable error caused by sample matrix and experiment operation, and the ultra-level of PGEs, a correction factor  $f_R$  was added to the equation (2) to obtain the equation (3).  $f_R$  is the average recovery ( $n = 3$ ) of the Pt, Pd and Rh in the spiked seawater (10 ng L<sup>-1</sup>) after a run of every 5 samples. If  $f_R$  is greater than 90%, it is believed that the enrichment system is operating normally. While  $75\% < f_R < 89\%$ , it is believed some errors may have occurred in the extraction, but the data is still credible after the correction by  $f_R$ . Once  $f_R$  is less than 75%, the recovery of Pt, Pd and Rh in the spiked seawater will be conducted for another three times. If the average recovery ( $n = 6$ ) is still less than 75%, the system is considered to have problems or the extraction exceeds

the load capacity of the resin, and the column must be replaced. The average recovery is calculated after a run of every 15 samples to one column. By the correction of the equations, it is easy to judge the stability of the experiment and more reliable results could be obtained.

$$F = \frac{M_S}{M_E} \quad (1)$$

$$C_S = \frac{C_E}{F} \quad (2)$$

$$f_R = \frac{R}{3} \quad (3)$$

$$C_{SC} = \frac{C_E}{f_R \times F} \quad (4)$$

F: the enrichment factor of the extraction;  $M_S$ : the mass of the sample;  $M_E$ : the mass of the elution;  $C_S$ : the concentration of PGEs in sample;  $C_E$ : the concentration of PGEs in eluent; R: the recovery of PGEs in spiked seawater (10 ng L<sup>-1</sup>) every 5 samples;  $f_R$ : the average recovery of standard addition sample of the PGEs-free seawater,  $n = 3$ ;  $C_{SC}$ : the concentration of PGEs in sample after correction.

## 2.6. Lab-prepared artificial reference materials

Two kinds of standard addition seawater samples, represented by AW and YW, were prepared in our research owing to the lack of commercially available reference materials in our lab.

The AW was prepared by standard addition to artificial seawater sample in which Pt, Pd and Rh were free. The artificial seawater was prepared according to the standard method D1141-98 (Reapproved 2013; American Society for Testing and Materials, ASTM). In order to get the quantitative and accurate spikes, 1, 10 and 100 µg L<sup>-1</sup> of the mixed stock 2% HNO<sub>3</sub> solutions of Pt, Pd and Rh were prepared



with serial dilution from 1000 mg L<sup>-1</sup> stock solution of these three elements and the precise concentrations were determined by ICP-MS. Then, the artificial standard seawater was spiked with different mixed stock solutions, and the final work concentrations of the standard samples were 0.1, 0.5, 1 and 10 ng L<sup>-1</sup>, respectively.

The YW was prepared according to the method proposed by Hatje et al. (2014). The seawater used for the preparation of the YW was collected from the North Yellow Sea in May 2015 (station B23 in Fig. 1). Prior to the preparation, the seawater was UV-digested and then cleaned with Nobias-chelate PA1<sup>®</sup> in pH = 7.0 ± 0.2 to ensure that no Pt, Pd and Rh were present. Afterwards, the seawater was acidified to pH = 2.0 ± 0.2 by adding ~1 mL concentrated HCl, and then stored in 1 L LDPE bottles. Similar to the preparation of AW reference materials, four standard spiked seawater samples were prepared. The recoveries of Pt, Pd and Rh in the lab-prepared artificial reference materials could not only help test the reliability of the extraction but also eliminate the interference caused by the difference in sample matrix. Furthermore, the use of the seawater standards for calibration, with quantitative recovery by the resin, eliminated the need to perform isotope dilution to account for variations in recovery of the resin (Biller and Bruland, 2012).

### 3. Results and discussion

#### 3.1. Blanks, detection limits, and interferences

The method blank of extraction mainly involved two aspects. One was the reagent blank, which was caused by the reagents used in the pre-concentration such as NH<sub>4</sub>OH buffer solution, HNO<sub>3</sub> and HCl. The other blank was the system blank, caused by the extraction system of the column, piping, other manifold and the instrument blank. The detection limits (LOD) for the PGEs were calculated based on 3σ (three times of the standard deviation of the blanks, n = 11), and the quantification limits (LOQ) were ten times of the σ (Table 1). The enrichment factor (F) of the extraction calculated by the ratio between the mass of sample and elution was 180–200.

The accurate detection of Pt, Pd and Rh using ICP-MS is often disturbed by physical interference, isobaric interferences, polyatomic interferences and matrix effects. The physical interference induced by instrument could be eliminated by the inner standard In. The matrix interferences were not taken into account because the PA1 resin does not adsorb the microelement e.g. Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> in seawater (Sohrin et al., 2008). Therefore, the interferences which hamper the accurate measurements of Pt, Pd and Rh are mainly from the isobaric elements and polyatomic interferences. The interferences on Pt are mainly from the element <sup>179</sup>Hf, e.g. the polyatomic HfO<sup>+</sup> has interference on all Pt isotopes (Fischer et al., 2018). However, there was no significant HfO<sup>+</sup> formation (<1%) under the instrument condition used in this study and the Hf ions in seawater was not adsorbed by the PA1 resin under the standard addition experiment. Hence, the data of Pt did not need to be corrected because the interference contribution of Hf was little. For Rh, the interference was controlled by monitored the signals of <sup>40</sup>Ar<sup>63</sup>Cu<sup>+</sup>, <sup>87</sup>Sr<sup>16</sup>O<sup>+</sup>, <sup>87</sup>Rb<sup>16</sup>O<sup>+</sup>, and <sup>206</sup>Pb<sup>2+</sup>. For Pd, a significant interference of <sup>68</sup>Zn and <sup>108</sup>Cd on <sup>108</sup>Pd, and <sup>106</sup>Cd and <sup>65</sup>Cu on <sup>105</sup>Pd was observed. These interferences derive from the polyatomic interferences of <sup>68</sup>Zn<sup>40</sup>Ar and <sup>65</sup>Cu<sup>40</sup>Ar and isobaric interferences of <sup>108</sup>Cd and <sup>106</sup>Cd. In order to obtain the accurate data, the following correction formula were used to eliminate the interferences.

$$I_{Pd} = I_{Pd,t} - I_{ZnAr} - I_{Cd} - I_{CuAr} \quad (6)$$

$$I_{Rh} = I_{Rh,t} - I_{CuAr} - I_{SrO} - I_{RbO} - I_{Pd} \quad (7)$$

In which,  $I_{Pd}$  and  $I_{Rh}$  are the correction concentrations of Pd and

Rh;  $I_{Pd,t}$  and  $I_{Rh,t}$  are the total concentrations of Pd and Rh, isobaric interferences, and polyatomic interferences;  $I_{ZnAr}$ ,  $I_{Cd}$ ,  $I_{CuAr}$ ,  $I_{SrO}$ ,  $I_{RbO}$ ,  $I_{Pd}$  are the concentrations of isobaric and polyatomic interferences.

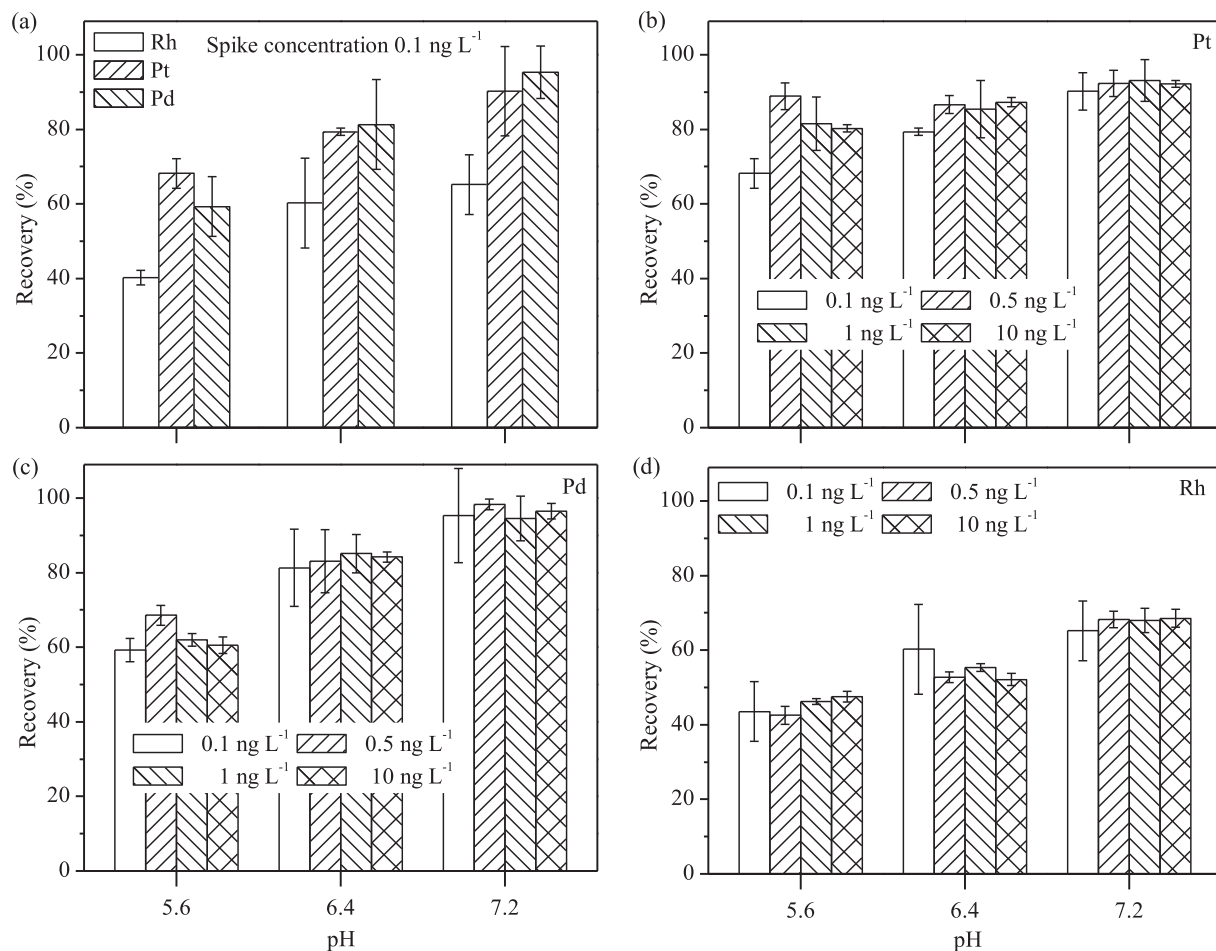
#### 3.2. pH conditions

pH is an important factor that affects the adsorption efficiency of the resin to the target element (Kaur et al., 2007; Sun et al., 2012). Several researchers demonstrate that Nobias-chelate PA1<sup>®</sup> resin exhibits an excellent adsorption capacity for many elements in a wide pH range 4–8 (Sohrin et al., 2008; Biller and Bruland, 2012). However, for Pt, Pd and Rh, the adsorption performance of PA1 resin exhibits a strong pH-dependence in QW (Sohrin et al., 2008). Therefore, the standard addition recoveries of Pt, Pd and Rh in the YW samples were conducted to obtain the optimum pH for the extraction method at a pH range 5.6–7.2. The recovery of each element was repeated 3 times with different pH in each. The various recoveries of Pt, Pd and Rh with different pH in each channel of the extraction manifold are shown in Fig. 3. It could be found that these elements exhibited diverse responses to their adsorption on the Nobias-chelate PA1<sup>®</sup> resin in this range of pH. Pt showed a high and stable recovery (85–95%), and the recovery of Pd increased with the change of pH to alkaline direction. In the low pH range about 5.6–6.4, the recovery of Pd was only 45–65%, and when the pH ≈ 7, the recovery could reach more than 90%. The recovery of Rh was consistently below 70%, and the values stabilized at approximately 65% at pH ≈ 7. In general, the highest recoveries of Pt, Pd and Rh were obtained at pH = 7.0 ± 0.2. Therefore, we chose this pH range as the optimum adsorption condition for the extraction method.

The factors controlling the adsorption capacity of the Nobias-chelate PA1<sup>®</sup> resin to PGEs are functional groups EDTriA and IDA (Supplementary Material Fig. S1). These two functional groups capture the target elements by forming the stable complexes with the -N: and -O<sup>-</sup> (Supplementary Material Fig. S1). However, it is difficult for these groups to destroy the chemical bond that have similar polarity e.g. OH<sup>-</sup>. Hence, the EDTriA and IDA may prefer to capture the PGEs ions complexing with Cl<sup>-</sup>, which results in the recovery of Rh being lower than Pt and Pd. The reason for this is that the complexes of Pt and Pd in seawater are mainly composed of [PtCl<sub>3</sub>OH<sup>2-</sup>]/[PtCl<sub>4</sub><sup>3-</sup>] and [PdCl<sub>3</sub>OH<sup>2-</sup>]/[PdCl<sub>4</sub><sup>3-</sup>] (Byrne and Yao, 2000; Colombo et al., 2008), while the complexes of Rh are dominated by Rh(OH)<sub>3</sub><sup>3-n</sup> (Gerber et al., 2010). Moreover, those complexes could transform significantly with the change of the pH. The complexes of PGE-OH increase with the pH of the seawater changing to the alkaline direction, and the complexes of PGE-Cl increase with the pH shifting to the acidic direction (Byrne and Yao, 2000; Colombo et al., 2008; Gerber et al., 2010). In the pH range selected in this study (5.6–7.2), the complexes of Pt and Rh are stable, while the complexes of Pd could undergo a dramatic change from Pd-Cl to Pd-Cl-OH (Byrne and Yao, 2000; Colombo et al., 2008). This may be the reason that the recovery of Pd showed a fluctuation with pH.

#### 3.3. Effects of the sample matrix

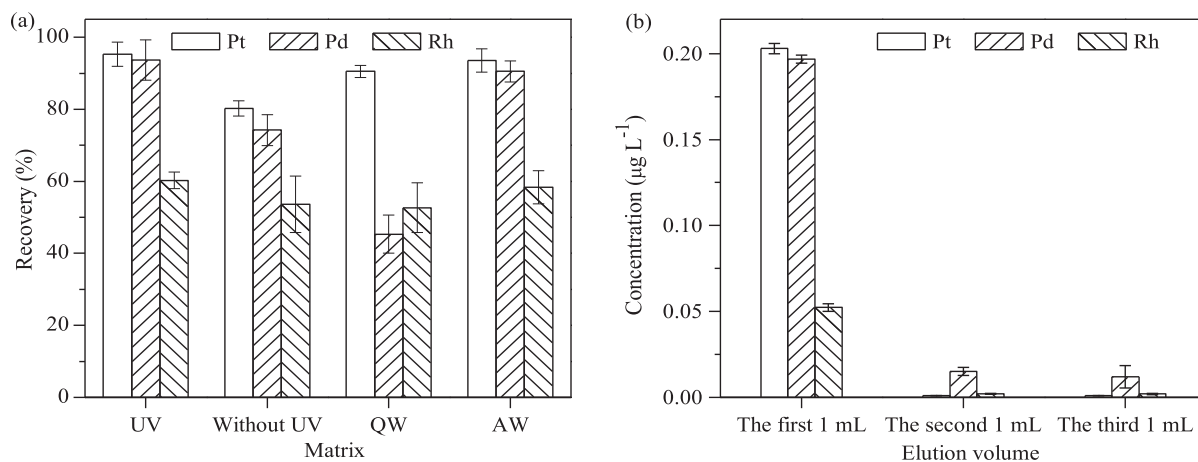
The sample matrix significantly determines the complex forms of Pt, Pd and Rh in seawater (Byrne and Yao, 2000; Colombo et al., 2008; Gerber et al., 2010). Previously, researchers thought that the complexes of PGEs in seawater were dominated by inorganic ligands (Colombo et al., 2008). However, recent studies demonstrated that PGEs could form stable complexes with the dissolved organic matter (DOM) (Turner et al., 2008; Cobelo-García, 2013). Moreover, researchers showed concerns that some organically bound elements (e.g. Cu and La) could lead to the low recovery of the Nobias-chelate PA1<sup>®</sup> resin (Biller and Bruland, 2012; Hatje et al.,



**Fig. 3.** Recoveries of Pt, Pd and Rh adsorption on the Nobias-chelate PA1® resin in the spiking experiments at the spike level of 0.1 ng L<sup>-1</sup> in the YW samples (a). Recoveries of Pt, Pd and Rh in different pH and spike concentrations in the YW samples are shown in (b), (c) and (d), respectively.

2014). Therefore, an ultraviolet irradiation pretreatment process to remove the DOM in the YW sample was conducted to investigate the interference of organic complexation on the extraction. This method is adequate to destroy metal-binding organic ligands for a range of trace metals (Milne et al., 2010; Biller and Bruland, 2012). In addition, controlled extraction experiments on Pt, Pd and Rh in artificial seawater without being UV-digested and PGEs-free

seawater were also carried out simultaneously. Fig. 4a shows the recoveries of Pt, Pd and Rh adsorption on Nobias-chelate PA1® resin under different pretreatment conditions. Various responses in recovery could be found for different elements and matrices, and the higher recovery was obtained in the experiments on the UV-digested samples. The recovery of the UV-treated samples was 117.6–137.9% of the untreated samples. Furthermore, a similar



**Fig. 4.** Recoveries of Pt, Pd and Rh adsorption on the Nobias-chelate PA1® resin in different matrices (a) and concentrations of Pt, Pd and Rh in the eluent of different elution steps in the spiking experiments at the spike level of 1 ng L<sup>-1</sup> each of them (b). UV: UV-irradiated seawater; Without UV: natural seawater; QW: ultra-pure deionized water; AW: artificial seawater.

recovery of Pt, Pd and Rh in the UV-treated samples and the artificial seawater samples was obtained (Fig. 4a). This evidence indicated that the organic matter in seawater might hamper the adsorption of PGEs on the Nobias-chelate PA1<sup>®</sup> resin.

Besides the aforementioned aspect, a reversal phenomenon was also found. The Nobias-chelate PA1<sup>®</sup> resin is expected to have a better adsorption performance on PGEs in the QW than in the seawater, because the QW contains no interference substances. However, the recovery of Pd in the QW was lower than in the seawater in this study. This phenomenon may result from the transformation of Pd complexes in different matrices. In the QW, the speciation of Pd is predominated by Pd-OH complexes according to the thermodynamic experiments and calculations (Byrne and Yao, 2000; Colombo et al., 2008). But with the increase of the concentration of chloride ions in the water, the form of Pd complexes changes from Pd-OH to Pd-OH-Cl. As that was mentioned above in section 3.2, thermodynamically, the former form was more stable than the latter. Hence, the functional groups on the resin could not effectively extract Pd in the QW samples resulting in a decrease of recovery. The chemical species changes of Pd and Rh in different environmental matrices are shown in Supplementary Material Fig. S2.

### 3.4. Effects of the sample and elution volume

Due to the low concentration of PGEs in seawater, which is approximately  $0.98 \text{ pmol kg}^{-1}$  (Ojeda and Rojas, 2007), a higher enrichment factor is highly beneficial for achieving a greater efficiency of extraction. Hence, it is necessary to control the mass ratio of the sample volume to the elution volume. According to the existing experimental conditions, increasing the sample volume would significantly extend the loading time and reduce the efficiency of extraction. On the other hand, if the volume of sample is too small (e.g. <100 mL), it is hard to get enough eluent with the expected degree of enrichment for instrument. Therefore, in this study, 200 and 150 mL seawater samples were selected to investigate the effect of the volume. As a result, it was found that the recovery of the 200 mL sample (~93%) was higher than the 150 mL (~82%). Although the exact reason for this is unclear, the ultra-low concentration of PGEs in the samples would be a key factor. Insufficient sample volume and ultra-low concentration increased the determination difficulty of the instrument and resulted in errors. Hence, 200 mL was a proper sample volume for the extraction.

To increase the enrichment factor, it is more convenient to control the eluent volume than sample volume. In previous studies with the similar extraction system, two sample-eluent ratios about 100 mL sample to 1 mL eluent (Biller and Bruland, 2012) and 70 mL sample to 0.4 mL eluent (Hatje et al., 2014) were used. Hence, a total of 3 mL eluent, added with 1 mL each time for 3 times, was used to elute the elements considering the larger volume of the samples in this study. Fig. 4b shows the concentrations of Pt, Pd and Rh in different sequentially added eluents. It could be found that more than 95% of the elements adsorbing on the resin were eluted at the first 1 mL eluent. In contrast, less than 3% of the elements were detected in the second and third 1 mL. Therefore, 1 mL eluent was enough to remove the Pt, Pd and Rh retained on the resin.

### 3.5. Recovery

The estimate of resin recovery was carried out by comparing the calibration slope of the seawater standard additions with the slope of 1 N HNO<sub>3</sub> standard for all metals, as that was described in Biller and Bruland (2012) and Hatje et al. (2014). In order to evaluate the interference caused by the difference among the extraction columns, the recoveries of Pt, Pd and Rh in every channel in the

experiments on the YW samples at different pH values were tested, and the results are shown in Supplementary Material Table S1. It was found that the differences in the recoveries gained from different columns were little. The recoveries of Pd and Pt were 94.5–98.3% and 93.3–98.3%, respectively, and Rh had the lowest values about 65.2–68.5%. These results were consistent with the discussion in sections 3.2 and 3.3. The data discrepancies among different elements might be caused by the chemical species of Pt, Pd and Rh in seawater, the stability of their complexes, and the polarity of the resin functional groups.

As discussed in section 3.2, the complexes of Rh in seawater might be dominated by Rh-OH under the optimum pH condition in the extraction of this research (Colombo et al., 2008). Nevertheless, the functional groups adsorbing Pt, Pd and Rh on the Nobias-chelate PA1<sup>®</sup> resin are mainly composed of N atoms and O atoms (Supplementary Material Fig. S1), which have similar polarity with OH<sup>-</sup>. Hence, the adsorption ability of Rh ions on the Nobias-chelate PA1<sup>®</sup> resin in seawater is lower than that of Pt and Pd ions. The excellent recovery of Pd adsorption on PA1 resin might result from the change in chemical species of this element. In QW, the complexes of Pd are mainly in the form of Pd-OH, which hindered the adsorption of the resin. However, with the increase of the concentration of chloride ions, the complexes of Pd changed from Pd-OH to Pd-Cl in seawater (Colombo et al., 2008). Hence, the recovery of Pd increased with the appearance of chemical bonds which could be destroyed more easily by the functional groups of PA1, but the complexes of Rh was still in Rh-OH form. For Pt, the chemical bonds of Pt-OH and Pt-Cl complex may be similar and weaker than Pd-OH-Cl and Rh-OH (Wood, 1991; Colombo et al., 2008; Bugarić et al., 2015). Hence, the resin exhibited different adsorption capacity for Pt, Pd and Rh in seawater.

### 3.6. Contrast with other methods

Although the detection of platinum group elements in seawater is challenging, researchers have proposed some solutions for this work. In order to evaluate the advantages and disadvantages of our extraction method, we compared similar solid-liquid extraction methods adopted in the publications.

Calvo Fornieles et al. (2016) proposed a method of extracting Pt, Pd and Ir in standard addition seawater by their own lab-prepared resin DPTH-gel and had an excellent detection limit about 1.4, 0.5 and  $0.6 \mu\text{g L}^{-1}$  Pt, Pd and Ir, respectively. The eluent volume of their method was 18 mL and the enrichment factor was 6.3–6.7. This enrichment factor is insufficient for extracting the ultra-concentration of PGEs in natural seawater. However, this resin showed excellent selectivity to PGEs in seawater and may have appreciative application prospect. For our method, only 1 mL of eluent was needed to remove more than 95% of the elements retained on the resin, and the enrichment factor could reach 180–200. This factor could effectively enrich Pt, Pd and Rh from natural seawater. Suzuki et al. (2014) used a commercially available resin AG<sup>®</sup> 1-X8 to extract Pt from seawater and achieved satisfactory results. The detection limit and process blank were very low, only 2.93 and  $1.95 \text{ pg L}^{-1}$ , and the enrichment factor could reach about 600-fold. However, the enrichment time of their method was about 24 h to one seawater sample, which may limit work efficiency in real application.

For our method, approximately 200 mL of sample was required, the extraction time of one sample was about 5 h, and multi-samples (>4) could be conducted simultaneously. Moreover, the eluent only needed one simple collection step in our method. The analytical performance data of this and related methods reported in the literature are listed in Table 2. It could be found that previous

**Table 2**  
Analytical performance information in different research.

Sample	Instrument	Extraction agent	Loading time	Enrichment factor	Detection limit (pg L <sup>-1</sup> )			Reference
					Pt	Pd	Rh	
Tokyo Bay water	ICP-MS	AG <sup>®</sup> 1X-8	8 h	~600	2.95	– <sup>a</sup>	–	Mashio et al. (2016)
Ocean water	GFAA	AG <sup>®</sup> 1X-8	>20 h	44.4	15	–	–	Hodge et al. (1986)
Ocean water	ICP-QMS	AG <sup>®</sup> 1X-8	8 h	~600	2.95	–	–	Suzuki et al. (2014)
Estuarine water	ID-ICP-MS	AG <sup>®</sup> 1X-8	6–24 h	200–250	1.87	–	–	Obata et al. (2006)
Seawater	ICP-OES	DPTH-gel	~1 h	6.7; 6.3	0.5 <sup>b</sup>	0.6 <sup>b</sup>	–	Calvo Fornieles et al. (2016)
Seawater	ICP-SFMS	Dowex <sup>®</sup> 1X8	~1 h	40	3.9	–	–	Fischer et al. (2018)
Coastal water	ICP-MS	Nobias-chelate PA1 <sup>®</sup>	~5 h	180–200	16.53	16.41	26.88	This work

<sup>a</sup> “–” represents no relevant reference data.

<sup>b</sup> In µg L<sup>-1</sup>.

**Table 3**

Concentration of Pt in different water samples. For the sake of comparison, the results in other literature were kept in line with the data of this study presenting in pmol kg<sup>-1</sup>.

Sample	Concentration of Pt (pmol kg <sup>-1</sup> )	Reference
Pacific Ocean water	0.19–1.13	Hodge et al. (1986); Suzuki et al. (2014)
Estuarine water	4.88–30.7	Obata et al. (2006)
River water	0.18–5.79	Soyol-Erdene and Huh (2012)
Tokyo Bay water	0.27–7.74	Mashio et al. (2016)
Otsuchi Bay water	0.60–14.2	Mashio et al. (2016)
Rain water	0.13–0.62	Mashio et al. (2016)
Coastal water	1.28–4.48	This study

methods have their own shortcomings, e.g. the longer loading time of sample, lower enrichment factor, and non-simultaneous-operation in other solid-phase extraction methods of PGEs in seawater (Hodge et al., 1986; Bertine et al., 1996; Mashio et al., 2016). In contrast, the off-line extraction method used in this study is easily controlled and the applicability is better than some on-line methods with ICP-MS. The on-line extraction method usually means longer working hours, which greatly affects instrument performance and increases operating costs. Therefore, the method used in this study was a low-cost way for simultaneous extraction of Pt, Pd and Rh in seawater.

### 3.7. Application to actual seawater samples

In this study, the method we built was used to investigate the concentrations of Pt, Pd and Rh in the surface seawater of 5 stations (3, 9, 15, S7 and S8 in Fig. 1) in the coastal area of the North Yellow Sea, and the data were compared with those reported in the literature. The concentrations of the three elements in the investigated coastal waters were low, with 1.31–4.59 pmol kg<sup>-1</sup> Pt, 0.97–1.41 pmol kg<sup>-1</sup> Pd and 0.16–0.42 pmol kg<sup>-1</sup> Rh (the actual concentration of Rh may have been underestimated because of its lower recovery, and the detailed data are shown in the Supplementary Material Table S2). Table 3 shows the concentrations of Pt in different natural water samples (there is a lack of the data for dissolved Pd in literature and the data of dissolved Rh was only obtained in Ocean water). Compared with the data obtained from the oceanic environment (Pt: 0.23–0.24 pmol kg<sup>-1</sup>, Suzuki et al., 2014; Rh: 0.3–0.9 pmol kg<sup>-1</sup>, Bertine et al., 1996), these elements had obvious enrichment in coastal waters. Their accumulation in coastal waters may come from both natural and anthropogenic sources through various channels and is a result of the interaction of many complicated biogeochemical processes. It was reported that the farther away from the city the lower concentration of Pt in the river (Cobelo-García, 2013), which shows a clear anthropogenic impact. In contrast, research indicated that the concentration of Pt (1.27–4.58 pmol kg<sup>-1</sup>) in the Tokyo Bay was higher than that in the water from the surrounding rivers

(0.29–1.46 pmol kg<sup>-1</sup>) (Obata et al., 2006; Mashio et al., 2016), so other factors rather than riverine discharge should be responsible for this. However, there is a lack of the data of dissolved Pd and Rh in rivers and seas, so more research is needed in future.

## 4. Conclusions

In this study, an off-line method for simultaneous extraction of Pt, Pd and Rh using chelate resin PA1 from seawater was built and tested. This method is simple to operate, could enrich multiple samples simultaneously, and has low detection limits and blanks. Excellent recoveries for Pt and Pd were obtained with this enrichment method, about 92.2–98.3% and 94.5–98.3%, respectively. However, the recovery of Rh was low, only 65.2–68.5%. Moreover, the use of lower volume of eluent allowed for this method achieving a high enrichment factor of about 200, which made the extraction of ultra-trace PGEs from seawater efficient. Due to the lack of commercially available reference materials in our lab, lab-prepared artificial standards were used in this research to validate the method. The detected values of Pt and Pd were consistent with the quantity spiked to the standards, but only two-thirds of Rh was recovered. This method has been successfully applied to the detection of Pt, Pd and Rh in actual seawater samples, and the data of Pt was consistent with the references. In summary, it is a feasible and promising method for the detection of dissolved platinum group elements in seawater.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2018.08.098>.

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