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Modified enrichment and purification protocol for dissolved silicon isotope determination in natural waters

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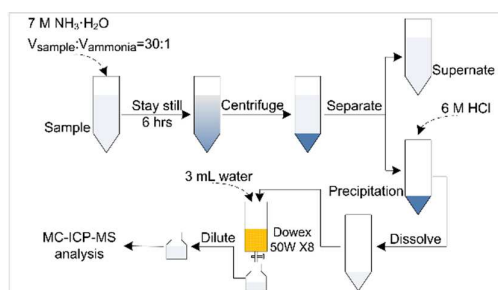
Single magnesium co-precipitation combined with resin separation to enrich and purify the dissolved silicon for the determination of silicon isotopes.

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Abstract:

Preparation of dissolved silicon in natural waters for the determination of silicon isotopes by MC-ICP-MS often involves the pre-concentration and purification steps. In this study, we present a simplified magnesium co-precipitation step to enrich the dissolved silicon by substituting concentrated ammonia for NaOH solution and increasing the co-precipitation time. Silicon recovery using single co-precipitation protocol is quantitative and less impacted by the volume of ammonia. Separation of silicon from other cations is achieved using a cation exchange resin and ensures complete yields. A low procedural blank of ~14.0 ng Si was achieved by purifying all the reagents. No detectable Si isotope fractionation was observed using the optimized single co-precipitation followed by cation exchange resin purification. Suitability for application of this method in different natural waters is demonstrated, including the river water, saline water and seawater. The modified single co-precipitation method presented in our study is more convenient than the previous multiple co-precipitation protocol, and has a broad application range.

1. Introduction

Dissolved silicon isotopic composition (commonly expressed in $\delta^{29}Si$ or $\delta^{30}Si$) of natural waters have been proved able to trace both biotic and abiotic cycles of silicon (Si) in the environment [1]. The development of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) provides a precise way to determine Si isotopes in a sub-permil level [2, 3]. Nevertheless, most of the water samples cannot be directly measured due to either low dissolved silicon (DSi) concentration and/or matrix effect, therefore pre-treatment steps are required prior to instrumental analysis.

Two protocols have been widely used to enrich and purify the DSi in seawater samples. First method is by quantitative precipitation of Si as triethylamine silico-molybdate (TEA-Moly precipitation), and followed by high temperature combustion and dissolution with HCl-HF mixture for instrumental isotopic analysis [4]. The main limitation of this protocol is the inefficient recovery for samples with DSi concentration below 10 μmol L^{-1}, thus additional pre-concentration steps are required in dealing with the open ocean surface samples . The other method to enrich DSi in the seawater offers the use of magnesium induced co-precipitation (MAGIC) through addition of alkali to form $Mg(OH)_2$ precipitate [5], and followed by a cation exchange resin separation [6]. Compared to the TEA-Moly precipitation method, this technique is HF-free and can be applied in samples with low DSi concentration (~1 μmol L^{-1}) [5]. Though, Reynolds et al. (2006) found that single co-precipitation using NaOH (1 mol L^{-1}) as the co-precipitator brought low Si recovery and significant Si isotope fractionation, in this case a two-stage co-precipitation process was required [5]. However, the multiple enrichment steps result in excess work of the whole pre-treatment procedures, and may induce more anionic matrix that is difficult to be separated by the following resin purification [6]. The combination of MAGIC and ion exchange resin technique has also been applied in river systems [7] which have relative high DSi concentration, but its applicability to low DSi freshwater has not been demonstrated. Unlike the river water and seawater which have a relative stable composition of major components, the estuarine water bodies show great change in ionic strength and chemical composition[8, 9], while few data on the dissolved Si isotopic composition in the estuary have been reported. A well-evaluated method that adapted to the determination of Si isotope in the high physical and chemical dynamic estuary region is required.

In this study, we report a modified magnesium co-precipitation method followed by a cation exchange resin separation step of DSi in

natural waters prior to isotopic determination by MC-ICP-MS. Complete Si recovery with the single pre-concentration and purification procedure is obtained, with inducing low procedural Si blank of ~14 ng. Suitability for application of this method in natural waters with different Si concentration and matrix composition has been tested on river water, saline water and seawater samples, resulting in quantitative Si recovery and no detectable silicon isotopic fractionation.

2. Experiments

2.1 Instrumental analysis

Si isotope analysis was performed by Neptune MC-ICP-MS (ThermoFisher, Germany). Sample solution was introduced in a dry plasma mode using an Apex-IR desolvating device, the heating and cooling temperature were set to 100 °C and 4 °C, respectively. The ion currents of all three Si isotopes were detected simultaneously in static mode, using a cup configuration of L3(^{28}Si)-L1(^{29}Si)-H3(^{30}Si). The polyatomic interferences were resolved by measuring at the lower mass side of ^{28}Si, ^{29}Si and ^{30}Si at medium resolution [10, 11]. Instrumental sensitivity for routine work was kept near 4.0~5.5 V ppm^{-1} on ^{28}Si, resulting in a signal of 2-3 V on ^{28}Si for a standard solution containing 500 ppb Si. Note that a much higher sensitivity (> 10 V ppm^{-1} on ^{28}Si) could be obtained by increasing the sample gas flow rate, but it was observed to greatly increase the intensity of NO^{+} and also cause larger shift in mass bias, thus a moderate sensitivity with optimal stability was preferred in our study. Instrumental blank obtained in Milli-Q water was as low as about 10 mV on ^{28}Si^{+}. Between runs the sample introduction system was rinsed with Milli-Q water, the washout process usually took 3 minutes after samples and 5 minutes after standards to allow the signal drop to below 1% of the sample intensity.

The data were collected in one block of 30 cycles, each with an integration time of 8 seconds per cycle. Typical internal standard deviation on one block of ^{29}Si/^{28}Si and ^{30}Si/^{28}Si were generally better than 1*10^{-5}. Instrumental mass bias and shift were corrected using a standard-sample bracketing (SSB) technique [6]. In order to assure identical mass bias, Si concentration of all standards and samples matched to within 20%. Si isotopic composition was expressed as deviations of ^{29}Si/^{28}Si and ^{30}Si/^{28}Si from NBS28 in parts per thousand and calculated as follows:

$$\delta^{x}Si(‰) = ((^{x}Si/^{28}Si)_{Sample}/(^{x}Si/^{28}Si)_{NBS28} - 1) \times 1000$$

in which x=29 or 30. During daily analysis, the silicon isotopic composition of two national reference materials GBW04421 and GBW04422 were checked prior to sample measurements. Long-term analysis of reference materials over 15 months gave an average δ^{29}Si and δ^{30}Si of 0.00±0.06‰ and −0.02±0.06‰ (2sd, n=20) for GBW04421 and -1.35±0.08‰ and -2.65±0.09‰ (2sd, n=20) for GBW04422, respectively. These values were in good agreement with the certified results determined by IRMS with fluorination [12].

Si concentration was measured with molybdenum blue method [13] on spectrophotometry with a continuous flow analyzer (Skalar SAN^{PLUS}). Mg concentration was determined on high resolution single collector inductively coupled plasma mass spectrometry (Element 2, ThermoFisher, Germany), with typical instrumental settings given by Tang et al. (2013) [14].

2.2 Reagents and standards

Hydrochloric acid used to clean the resin and dissolve the precipitate was sub-stilled twice. NH$_3$·H$_2$O was purified using isothermal distillation at room temperature for one week, the concentration of purified ammonia was about 7 mol L^{-1}. MgSO$_4$ solution (1 mol L^{-1}) was purified by adding 1% (v:v) NH$_3$·H$_2$O, the supernatant was transferred into clean LDPE bottle after centrifugation. All the dilution and cleaning procedures were carried out with deionized Milli-Q water.

Three Si isotope reference materials (NBS28, GBW04421 and GBW04422) were prepared using the alkaline fusion technique [6]. ~214.8 mg silicon reference material and ~757.1 mg Na$_2$CO$_3$ solid were taken and mixed in a platinum crucible; the mixture was fused in the muffle furnace at 950 °C for 1 hour; after cooling, the fusion cake was dissolved with 1 mol L^{-1} HCl and diluted to 100 mL in plastic volumetric flask; then, the solution was transferred into clean HDPE bottle and stored at 4 °C.

Besides, one river sample (RW-1) collected from the Yangtze River and two seawater samples (SW-1 and SW-2) collected from the East China Sea were used to examine the applicability of the pretreat method to different water bodies. Waters were collected and

filtered immediately with 0.4 μm PC membranes, the filtration was acidified to pH=2 with HCl and stored in pre-cleaned HDPE bottles at room temperature. DSi concentration of these three sample was measured to be 111.7 μmol L^{-1} for RW-1, 1.77 μmol L^{-1} for SW-1 and 1.75 μmol L^{-1} for SW-2. In addition, four saline waters with different DSi and ionic strength were prepared by mixing the seawater with the fresh river water or Si reference material GBW04422 (initial Si concentration was 2.5 μmol L^{-1}).

Table 1 Detailed information of the natural waters in this study

Sample NO.	Sampling location or preparation	Salinity	DSi (μmol L^{-1})
SW-1	East China Sea (125.34°E, 26.67°N)	35	1.77
SW-2	East China Sea (126.12°E, 26.97°N)	35	1.75
RW-1	Changjiang (121.03°E, 31.77°N)	0	111.7
Saline-1	V_{SW-1}: V_{RW-1} = 10:25	10	80.29 [a]
Saline-2	V_{SW-1}: V_{RW-1} = 20:15	20	48.88 [a]
Saline-3	V_{SW-2}: $V_{GBW04422}$ = 20:15	10	2.28 [a]
Saline-4	V_{SW-2}: $V_{GBW04422}$ = 10:25	20	2.07 [a]

[a] the DSi concentration of the saline waters was calculated based on the DSi of the endmembers.

2.3 Magnesium co-precipitation enrichment and cation exchange resin purification

In order to examine the Si recovery in the co-precipitation step, brucite precipitation was conducted by adding 1 mol L^{-1} NaOH or purified ammonia to seawater samples containing low (~5 μmol L^{-1}) and high (~5 μmol L^{-1}) content of Si. The volume ratio of sample to alkali was controlled to range from 100:1 to 2:1 for NaOH and from 50:1 to 1:1 for ammonia, respectively. The solution was shaken and kept undisturbed for 12 hours, followed by centrifugation at a relative centrifugal force of 2.22*10^3 g. The precipitate was dissolved with minimal amount of 6 mol L^{-1} HCl. Recovered Si content was determined after dilution with Milli-Q water. Besides, the effect of co-precipitation duration on the Si recovery was also checked with fixed sample to ammonia volume ratio of 30:1.

The cation exchange chromatographic method was adapted from Georg et al. (2006) [6] to remove large amount of Mg^{2+} in the solution prior to isotope determination. The column comprised a 6 mL polypropylene SPE tube, a polyethylene frit with 20 μm porosity and a polypropylene stopcock fitted to the outlet of the tube to adjust the flow rate. The operation adsorption capacity of resin (Dowex 50W-X8, 200-400 mesh, Sigma-Aldrich, USA) was measured to be ~2.1 meq mL^{-1} (wet resin) with acid concentration ≤ 0.1 mol L^{-1}, and the adsorption of Mg was completely when the elution flow rate ranged from 0.04 to 2.0 mL min^{-1}. Solution containing Mg and Si was loaded onto the column filled with 3 mL wet resin, and washed with Milli-Q water. The resin was regenerated with 12 mL 6 mol/L HCl and washed to neutral with Milli-Q water for reuse.

The potential isotope fractionation during the co-precipitation and resin separation step was demonstrated by applying the pretreatment method to Si reference materials with known isotopic value. During this step an addition of 1 mol L^{-1} MgSO$_4$ solution by volume ratio of 20:1 was required before co-precipitation. Besides, the pretreatment method was also applied to the natural waters containing varying amount of Si as well as matrix components. As the true values of river waters and seawaters were unknown, a double co-precipitation stage was conducted to check whether any Si isotope fractionation during the first enrichment step as pointed by Reynolds et al. (2006). The amount of ammonia used in the first and second co-precipitation step was identical. After dissolving with HCl, the solution was merged together and then proceeded to resin separation.

3 Results and discussion

3.1 Yield of chemical pre-treatment steps

Si could be quantitatively recovered by addition of ammonia with $V_{ammonia}$:V_{sample} of 1:30, the recovery for the low and high Si seawater averaged 98.0±0.3% (n=3) and 100.7±1.3% (n=3), respectively. However, inefficient Si recovery was observed when

substituting 1 mol L^{-1} NaOH for ammonia to co-precipitate the low Si seawater, and more than 20% of Si was lost during the co-precipitation. This incomplete recovery of Si using NaOH have also been previously reported by Reynolds et al. (2006) [5] and later by Cao et al. (2012) [15]. For high DSi seawater, Si recovery reached to 98.5% when NaOH was added with V_{NaOH}:V_{sample} ratio of 0.1, this ratio was close that used by Beucher et al. (2008) [16] but much higher than that used by Reynolds et al. (2006) [5].

Besides, it was observed that the Si recovery remained rather stable with increasing the $V_{NH_3 \cdot H_2O}$:V_{sample} from 0.03 to 1.0, indicating that excess ammonia would not affect the adsorption of Si onto the brucite. However, for high DSi seawater, the recovery decreased by 10% when increasing the V_{NaOH}:V_{sample} from 0.1 to 0.5 (**Figure 1a**). The loss of Si with addition of excess NaOH is probably caused by the competitive adsorption of excess OH$^-$. Considering the Mg concentration in the seawater ~0.05 mol L^{-1}, addition of 1 mol L^{-1} NaOH in the volume ratio of 0.1 has capacity of precipitating nearly all the Mg in the solution in the form of Mg(OH)$_2$. In this case, continuously adding NaOH will dissociate more OH$^-$ and increase the pH value of the solution, then the excess OH$^-$ may replace the SiO$_3^{2-}$ ions which have already been adsorbed on the precipitation. Nevertheless, the sample solution would behave as a buffering system and remain more stable when excess ammonia is added. As a result, Si recovery is less impacted by the volume of ammonia.

The co-precipitation duration was also proved to have impact on the recovery of Si. As shown in **Figure 1b**, Si of low DSi seawater was fully recovered when co-precipitating for half hour, with a recovery of 99.4±1.0% (2sd, n=3). During the same period, Si recovery of high DSi seawater was only 91.7±0.6% (2sd, n=3), and it increased to 100.2±1.6% (2sd, n=3) when extended the reaction time to 6 hours, indicated that longer reaction time allowed to form thorough precipitation and enhanced the removal of Si along with the precipitation of Brucite. Based on the results above, all the co-precipitation experiments in the following discussions were carried out by adding ammonia with volume ratio of 1:30 and kept undisturbed for 6 hours for full adsorption of Si.

Given the operation capacity of the cation resin was ~2.1 meq mL^{-1}, the pre-treatment method proposed here can process at least 65 mL seawater samples (suppose all Mg is precipitated as Mg(OH)$_2$). As for natural samples, normally about 4 mL solution would be obtained after enrichment and purification steps. Thus, the enrichment factor of the pre-treatment protocol can reach up to ~16 times. In another world, the pre-concentration and resin purification protocol can be applied to samples with initial Si concentration of ~1 μmol L^{-1}. Higher enrichment factor can be achieved by either increasing the resin volume or evaporating the eluted solution to a smaller sample size [17].

3.2 Procedural blank

Blank measurements were performed by applying the enrichment and resin purification protocol to 10 blank samples of 30 mL 0.01 mol L^{-1} HCl. 1.5 mL 1 mol L^{-1} MgSO$_4$ and 1.0 mL ammonia were used for each sample to conduct the brucite. Si blank values ranged between 12.8-15.9 ng for nine of the samples, with another value of 19.3 ng which was proved abnormal by Grubbs' test method at 95% confidence interval and Q test at 90% confidence interval. The average procedural blank was calculated to be 14.0±2.7 ng (2sd, n=9), lower than all the previous reported values of 30 ~ 800 ng [2, 18]. Due to the pre-purification of all the reagents (including the HCl, ammonia and MgSO$_4$), Si blank contributed by the reagents was almost negligible (<1 ng). This low level of procedural blank allows analyzing samples with small amount of Si.

3.3 Impact of pre-treatment protocols on silicon isotopes

3.3.1 Resin separation

The measured δ^{30}Si of GBW04422 after resin purification was -2.67±0.08‰ (1sd, n=5), which was consistent with the certified value of -2.65±0.04‰ [19]. This result confirms that the resin separation does not induce noticeable silicon isotope fractionation. Compare the δ^{30}Si of GBW04422 and RW-1 determined before and after the resin separation, it was found that the δ^{30}Si with and without resin purification was identical within analytical precision (0.06-0.10‰, 2sd), indicating that the presence of low content of metallic matrix will not exert significant influence on the silicon isotope measurement. Therefore, river water can be determined for silicon isotopes after simply dilution step. While it is worth mentioning that, in some cases the content of dissolved salt in the river water can be

significantly higher, such as there is significant evaporates in the drainage area [20], in such case it is desired to use resin separation prior to instrumental analysis.

Table 2 Measured $\delta^{30}Si$ of Si reference material GBW04422 and natural waters after different pre-treatment steps. The calculated $\delta^{30}Si$ of the saline waters was based on the mixed volume ratio (Table 1) and the isotopic composition of the seawater and fresh water end-members. Mg concentration for all the samples was matched to ~0.05 mol L^{-1} prior to co-precipitation via addition of $MgSO_4$. The italic number in the parenthesis denoted the number of measurements.

	Dilution or calculated	Resin	Single co-pre. + Resin	Double co-pre. + Resin
GBW04422	-2.65±0.05(*20*)	-2.67±0.08(*5*)	-2.61±0.04(*5*, C_0=2.5 µmol L^{-1}) -2.66±0.09(*5*, C_0=25 µmol L^{-1})	
RW-1	+1.89±0.07(*7*)	+1.84±0.04(*7*)	+1.86±0.09(*3*)	+1.87±0.08(*3*)
SW-1			+2.53±0.13(*3*)	+2.52±0.14(*3*)
SW-2			+1.75±0.09(*3*)	+1.78±0.11(*3*)
Saline-1	+1.86±0.06(cal.)		+1.87±0.08(*3*)	
Saline-2	+1.87±0.06(cal.)		+1.89±0.03(*3*)	
Saline-3	-1.69±0.06(cal.)		-1.72±0.11(*3*)	
Saline-4	-0.52±0.07(cal.)		-0.58±0.10(*3*)	

3.3.2 Mg(OH)$_2$ co-precipitation

$\delta^{30}Si$ was also measured for both the reference material and natural waters after being processed with single co-precipitation and resin separation protocol. As shown in Table 2, the measured $\delta^{30}Si$ of GBW04422 and RW-1 showed no obvious difference from the results obtained from dilution and resin separation, indicating that Si could be quantitatively recovered using single co-precipitation step, without any detectable silicon isotope fractionation.

As for the seawater samples, the measured $\delta^{30}Si$ after single co-precipitation and resin separation was +2.53±0.13‰ (1sd, n=3) for SW-1 and +1.75±0.09‰ (1sd, n=3), respectively. These values were in the same range of previously reported results for the global ocean [5, 21]. Contrasting to the work of Reynolds et al. (2006) who observed significant silicon fractionation using single co-precipitation stage, we found that the single and double co-precipitation protocols yielded nearly identical $\delta^{30}Si$ values, with difference of 0.03‰ at most (Table 2). Similarly, the $\delta^{30}Si$ of RW-1 processed with double co-precipitation step was consistent with the single enrichment technique. The guaranteed consistency of measured $\delta^{30}Si$ between single and double co-precipitation procedure further confirms that using ammonia as the co-precipitator can fully recover the dissolved silicon in the natural waters within single co-precipitation.

The combined mean $\delta^{30}Si$ from different pretreatment methods for the river water and seawater are +1.86±0.06‰ (1sd, n=20) for RW-1, +2.52±0.13‰ (1sd, n=6) for SW-1 and +1.76±0.10‰ (1sd, n=6) for SW-2, respectively. Based on the Si concentration and $\delta^{30}Si$ of the end-members, the $\delta^{30}Si$ of the four saline waters was theoretically calculated to range from -0.52‰ to +1.87‰ (Table 2). Meanwhile, the $\delta^{30}Si$ was also measured after single co-precipitation and resin separation. It turns out that the measured $\delta^{30}Si$ well matches with the calculated values, indicating that this method can be well applied in the preparation of saline water for silicon isotope determination.

4. Conclusions

In this study, we have presented a robust method to concentrate and purify the dissolved silicon in natural waters for the determination of silicon isotopes by MC-ICP-MS. The impacts of co-precipitator and reaction duration on the silicon recovery were tested. The results showed that using ammonia as the co-precipitator can provide higher and more stable silicon recovery than using NaOH, and

lengthening the co-precipitation time to 6 hours can assure complete removal of silicon from the solution. The procedural silicon blank obtained in this study was approximately 14 ng, and it was lower than all the previous studies to our knowledge. The tests of Si reference material demonstrated that the combination of modified single co-precipitation and resin separation technique would bring no obvious silicon isotope fractionation. Besides, the modified method is also proved suitable for the determination of silicon isotope ratios in natural samples containing varied silicon concentration and matrix composition, without bringing detectable silicon isotope fractionation. Application of this method presented here in different natural waters can provide insightful information about the silicon cycles in the natural environment.

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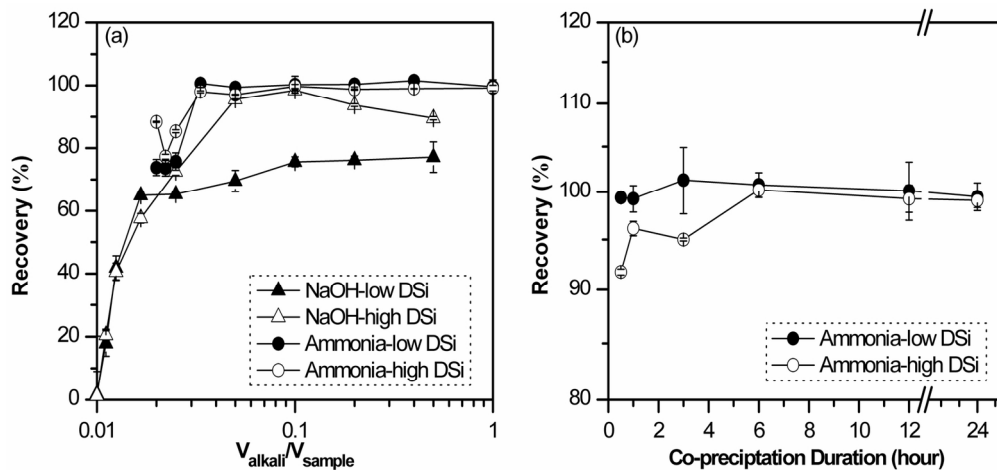
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Figure 1 Si recovery during the co-precipitation step with (a) varied alkali addition amount and (b) co-precipitation duration

The elution curve of Si during the resin separation was illustrated in Figure 2. In the sample loading stage, Si content in the first
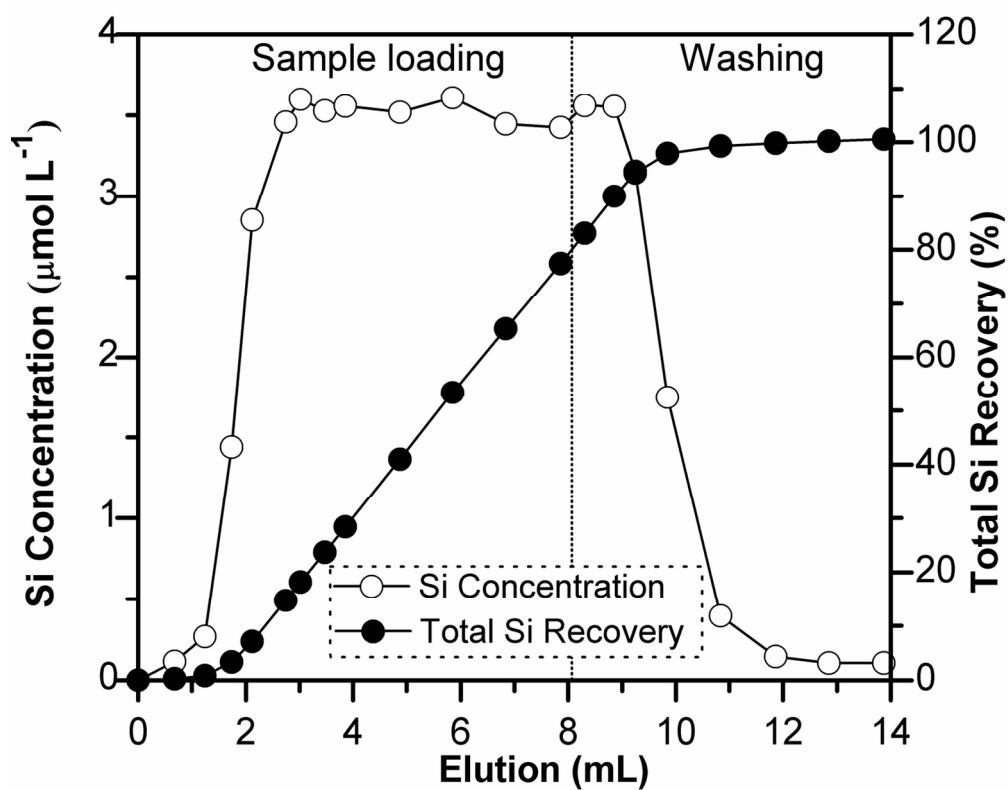
milliliter elution was quite low due to Si diffusion process in the residual pore water of resin column, and it quickly increased to the level of the original sample solution in the following fractions. As acid will impair the bonding strength between the resin and the metal ions, 1 mL×6 Milli-Q water was used to wash Si from the column. During this stage, Si was fully eluted within the first 3 mL Milli-Q water, the accumulative recovery of Si in the sample loading stage and the first 3 mL washing elution reached up > 99%.

Figure 2 Elution curve and accumulated recovery of Si in the cation exchange resin separation step. The original Si concentration in the solution was 3.58 μmol L^{-1} (100 ppb).

75x35mm (600 x 600 DPI)

66x53mm (600 x 600 DPI)