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Separation of trace amounts of Ga and Ge in aqueous solution using nano-particles micro-column

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ABSTRACT

A simple and rapid analytical method for the separation of trace amounts of gallium and germanium from aqueous solution by solid-phase extraction with nano-particles was developed. It was found that only Ga(III) could be quantitatively retained on nano-SiO_2 in the pH range of 3–4 and 8–12 while Ge(IV) was not adsorbed, but both Ga(III) and Ge(IV) ions could be adsorbed quantitatively on nano-TiO_2 within the pH range of 4–11. These two ions adsorbed by nano-particles could be desorbed quantitatively. Effects of acidity, concentration of elution solution and interfering ions on the recovery of the analytes were systematically investigated. The sorption data could be well interpreted by the Langmuir model. Based on the Langmuir model equation, the monolayer adsorption capacity of nano-SiO_2/nano-TiO_2 was calculated to be 4.26 mg g^{-1}/19.68 mg g^{-1} for Ga(III)/Ge(IV). Moreover, thermodynamic functions, the change of free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) of the adsorption reaction were estimated for each metal ion. Experimental data were also evaluated in terms of kinetic characteristics of adsorption and the adsorption process for both metal ions followed well pseudo-second-order kinetics. Finally, the proposed method was applied to the determination of trace Ga(III) and Ge(IV) in some water samples using loaded nano-particles columns, and it is found that the recoveries of Ga(III) and Ge(IV) were obtained to be in the range of 96.4–105.0%. And the method was validated with certified reference material (GBW07311, GBW 07406) and the values obtained for Ga(III) and Ge(IV) were in good agreement with the certified values.

1. Introduction

Gallium and germanium are rare elements, which have not been found free in nature, their compounds are widely disseminated in the earth's crust. Gallium occurs in very small amounts in rocks and ores of other metals, and gallium is mostly associated with aluminum, zinc, and germanium [1]. Germanium is found in ore deposits, mainly as a substitute for Zn in sphalerite, but also in Cu, Ag, Fe, Ge sulfides such as germanite, argyrodite, renierite, briarite and canfeldite [2]. Gallium and germanium compounds have been widely used in various fields of industry, such as GaAs, GaN, and GeO_2 for the manufacture of high technological optical devices, semiconductors, DVDs and laser diodes [3,4]. Their high market price has increased the interest from the industry, so researchers have focused their work on developing novel methods for separating and recovering Ga and Ge [5]. In general, mutual separation of semimetals, such as gallium and germanium, is difficult because of their similar behavior, low concentrations and matrix effects in aqueous solutions.

Generally solvent extraction plays an important role as a separation and concentration technique. The use of high-molecular weight amines, organophosphorus compounds such as sodium di-*n*-alkyl phosphinates [6,7], trioctylphosphine oxide (TOPO) [8,9], and di-(2-ethylhexyl phosphoric acid) (D2EHPA) [10] were used for gallium extraction. Germanium was also separated using extraction methods [11,12]. However, these research works on gallium and germanium ions are mainly focused on single element. Recently, multi-elemental separation has gained great interest in analytical chemistry. The density fractionation and sequential extractions are two most widely used methods for Ga and Ge separation [13]. But the operation process of the density fractionation methods was complicated. The extraction process was slow and also dangerous due to the use of a flammable organic phase, and the extraction processes cannot work at high temperature, as the solvents are generally volatile.

Besides, some solid sorbents have been also used for the separation and preconcentration of inorganic gallium or germanium. The adsorption capacity for Ge(IV) was 9.3 mg g^{-1} on active carbon [14], 130.8 mg g^{-1} on cellulose [15], and about 1.0 mg g^{-1} on mercapto-modified silica gel [16]; the adsorption capacity for Ga(III) was found to be 42 mg g^{-1} on polyurethane foam (PUF) [17]. Nano-particles as sorbents for separation of trace elements are an increasing interest owing to its effectiveness [18,19]. However,

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to the best of our knowledge, until now there is no report on the application of nano-particles for continuous separating Ga(III) and Ge(IV) ions in aqueous solution. The aim of this work was to develop a sensitive, rapid and simple method for the separation trace amounts of Ga(III) and Ge(IV) in aqueous solution using micro-columns packed with nanometer sized TiO_2/SiO_2. The optimized experimental conditions for the separation process were established. The adsorption data were fitted to various equations to obtain constants related to the equilibrium and kinetics of the adsorption. The proposed method was applied for separation of Ga(III) and Ge(IV) in some water and ore samples.

2. Experimental

2.1. Apparatus

Cary 5000 UV-vis-NIR spectrophotometer (Varian Company, USA) was used for the determination of Ga(III) and Ge(IV) ions. Mettler Toledo 320-S pH meter instrument (Shanghai Co. LTD, China) was used for pH measurements. KQ-100 Controllable Serial-Ultrasonics apparatus (Kunshan Apparatus Company, China) was applied to disperse sorbents in solution, operating at an ultrasonic frequency of 20–80 kHz and an output power between 0 and 50 W through manual adjustment. Model TDL80-2B centrifugal machine (Shanghai Anting Scientific Instrument Co., China) was used throughout. A HL-2 peristaltic pump (Shanghai Qingpu Instrument Factory, China) was used in separation and preconcentration process. A self-made PTFE micro-column (30 mm × 3.0 mm i.d.) was used.

2.2. Materials and reagents

Nano-TiO_2 and nano-SiO_2 were purchased from Zhoushanmingri Nanometer Material Company (China), and their particles sizes were about 10–30 nm.

The certified reference materials (GBW07311 stream sediment, GBW07406 soil) were provided by the State Technology Supervision Administration Bureau (China).

All of the other reagents including salicyl fluorone (SAF, 1.0×10^{-3} mol L^{-1}), phenyl fluorine (PF) alcohol solution (0.2 g L^{-1}), cetyltrimethyl ammonium bromide (CTMAB, 1.0×10^{-2} mol L^{-1}), acetic acid–sodium acetate (HAc–NaAc) buffer solution (pH = 6.0), sodium hydroxide, hydroxylamine hydrochloride, were of analytical reagent grade and purchased from Shanghai Xinzhong Chemical Reagent Co., China.

A 0.3 mol L^{-1} K_3PO_4 solution in 1.0 mol L^{-1} H_2SO_4 medium was prepared by dissolving 6.368 g of K_3PO_4 (Shanghai Chemistry Reagent Company, China) in 5.6 mL of concentrated sulfuric acid, then diluting to 100 mL with water.

The stock solutions of the various metal ions (mg mL^{-1}) were prepared with their nitrate or chloride salts (≥99.99%) and used to investigate the possible effects of interfering ions. Doubly distilled water was used throughout the experiments.

2.3. Column preparation

A total of 50 mg of nano-TiO_2/nano-SiO_2 was filled into a PTFE micro-column (30 mm × 3.0 mm i.d.), plugged with a small portion of glass wool at both ends. Before use, the column was conditioned to the desired pH with HCl and NaOH solutions.

2.4. Preparation of standard solutions of Ga(III)/Ge(IV) and their determination

A standard stock solution of Ge(IV) (1000 mg L^{-1}) was prepared by dissolving 1.4420 g GeO_2 (obtained from Beijing NCS Analytical Instruments Co., China) in 10 mL of 0.01 mol L^{-1} NaOH solution, then heating until the solution becomes transparent, finally diluting to 1000 mL with doubly distilled water.

A standard stock solution of Ga(III) (1000 mg L^{-1}) was prepared by dissolving 1.3440 g of Ga_2O_3 (obtained from Beijing NCS Analytical Instruments Co., China) in 30 mL of 6 mol L^{-1} HCl solution, and heating until the solution becomes transparent, and then diluting to 1000 mL with doubly distilled water.

The standard stock solutions of Ge(IV) and Ga(III) will be diluted successively to the required concentration in the experiment.

Determination of Ga(III) [20]: Aliquots of a standard solution containing 1–10 μg of Ga(III) were transferred into a series of 25 mL volumetric flasks followed by the addition of 3.5 mL of HAc–NaAc buffer solutions, 1.0 mL of 0.2 g L^{-1} PF, 3.0 mL of 1.0×10^{-2} mol L^{-1} CTMAB and then diluting to 25 mL with doubly distilled water. After 10 min, the concentration of Ga(III) was determined using a UV–vis–NIR spectrometer at wavelength of 563 nm with 1 cm quartz cell, and the content of Ga(III) was obtained.

Determination of Ge(IV) [21]: Aliquots of a standard solution containing 1–6 μg of Ge(IV) were transferred into a series of 25 mL volumetric flasks followed by the addition of 5.0 mL of 5.0 mol L^{-1} HCl, 2.0 mL of 1.0×10^{-3} mol L^{-1} SAF, 2.0 mL of 1.0×10^{-2} mol L^{-1}CTMAB and then diluting to 25 mL with doubly distilled water. After 10 min, the concentration of Ge(IV) was determined using a UV–vis–NIR spectrometer at wavelength of 505 nm with 1 cm quartz cell.

2.5. Procedure

2.5.1. Static batch experiments

The sorption experiments were carried out using a series of 50 mL flasks containing 0.05 g sorbents and 10.0 mL of 10 mg L^{-1} gallium/germanium solution at appropriate pH. If necessary, the pH of the solution was adjusted by addition of HCl or NaOH solution before the addition of sorbents. After ultrasonic dispersion for 4 min, the solid/liquid phases were separated by centrifuging at 4000 rpm for 5 min. The solutions were immediately analyzed for the determination of Ga(III)/Ge(IV) concentration.

The adsorption percentage (*Ads.%*) was calculated based on the following equation [22]:

$$Ads.\% = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

where C_0 and C_e are the initial and the final concentrations of the target analytes in solution phase, respectively.

The adsorption capacity of sorbents was calculated based on the following equation [22]:

$$q = \frac{V \times (C_0 - C_e)}{m} \qquad (2)$$

where q is the adsorption capacity of sorbents (mg g^{-1}); V is the volume of the solution in L; m is the mass of added sorbent in g.

Adsorption isotherm studies were carried out with initial concentrations of the target analytes varying between 10 and 240 mg L^{-1}, the sorbents amount was kept constant (0.05 g) and the experimental temperatures were controlled at 275, 298 and 323 K, respectively. The thermodynamic parameters for the adsorption process were determined at each temperature. An experiment without sorbents was carried out confirming that no adsorption occurred on the container wall.

Kinetic experiments were performed using a series of 50 mL flasks containing 0.05 g sorbents and 10.0 mL of 20 mg L^{-1} Ga(III)/Ge(IV) solution at appropriate pH in a temperature range of 275–323 K. On regular time intervals, suitable aliquots were taken, then the concentrations of Ga(III) and Ge(IV) were determined. The rate constants were calculated using the conventional rate expression.

2.5.2. Separation procedure of column

A solution containing 10 μg mL^{-1} Ga(III) and Ge(IV) was prepared, and the pH value was adjusted to 3.5 with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH. The solution was passed through the nano-SiO_2 packed micro-column by using a peristaltic pump at a desired flow rate. Ge(IV), which could not be retained by the column, passed directly through the column and the effluent solution from the nano-SiO_2 column was collected; while Ga(III) retained by the column, was eluted with 1.0 mL of 1.0 mol L^{-1} HNO_3 solution. If the matrix of samples is complex, the pH value of the effluent solution containing Ge(IV) ions is adjusted to 4.0–5.0, then the solution is passed through the nano-TiO_2 column. The retained Ge(IV) ions are eluted with 2.0 mL of $K_3PO_4 + H_2SO_4$ solution. Finally, the concentrations of the separated Ga(III) and Ge(IV) in the final solutions were determined by spectrophotometry.

2.6. Sample preparation

2.6.1. Water samples

Three synthetic water samples and the industrial effluent samples from a metallurgical plant were also analyzed. Suitable amounts of 1.0 mol L^{-1} HCl were added to adjust the acidity of samples pH 2 for storage. The samples were stored at 4 °C in low-density polyethylene (LDPE) bottles when the analysis of water samples was not carried out. The storage period was kept as short as possible.

2.6.2. Environment samples

Portions (1.000 g) of samples (GBW07311 stream sediment/GBW07406 soil) were decomposed with aqua regia (30 mL), heated until the solution becomes transparent, continuously heated to near dryness. Then 10 mL of H_2SO_4 (1:1), 10 mL of HF and 10 mL of HBr were added, and the samples were heated to emit white smoke. The residue was dissolved with 5 mL of 12 mol L^{-1} HCl, and heated to about 110 °C for 30 min, finally diluted to 100 mL with water. pH 3.5 of the solution was adjusted by addition of HCl or NaOH solution before the addition of sorbents. A blank experiment is also performed simultaneously under similar conditions.

3. Results and discussion

3.1. Selection of sorbents

The effects of different sorbents on the adsorption efficiency for gallium or germanium in aqueous solutions were studied and the result was listed in Table 1. It was found that the nano-TiO_2 (anatase) could quantitatively adsorb Ga(III) and Ge(IV) ions, but the nano-SiO_2 could only quantitatively adsorb Ga(III) ions. So they were chosen as sorbents for the separation/preconcentration of Ga(III) and Ge(IV) in the experiment.

Table 1
Effect of the different sorbents on adsorption efficiency of Ga(III) and Ge (IV).

Sorbents	Ads.%/Ge(IV)	Ads.%/Ga(III)
Nano-TiO_2 (anatase, 10–15 nm)	96.6	96.3
Micron-TiO_2	1.9	85.7
Nano-SiO_2 (20 nm)	0.1	97.4
Micron-SiO_2	0.0	63.0

Data indicate that model parameters are statistically significant (t-test) at 95% confidence level.

3.2. Static batch procedures

3.2.1. Effect of pH

In order to evaluate the effect of pH, the pH values of sample solutions were adjusted to a range of 1–14 with HCl or NaOH. To attain enough sensitivity, the standard solutions containing 10 mgL^{-1} of Ga(III) or Ge(IV) at different pH values were used. The nano-SiO_2/nano-TiO_2 was employed to separate and preconcentrate Ga(III)/Ge(IV). Fig. 1 is the effect of pH on the recoveries of Ga(III) and Ge(IV). It is clear from Fig. 1 that the Ga(III) could be adsorbed quantitatively (>95%) by nano-SiO_2 in the pH range of 3.0–4.0 and 8–12 while Ge(IV) could not be retained on nano-SiO_2 at pH 3–12. On the contrary, nano-TiO_2 could quantitatively adsorb Ge(IV) at pH 4–12. This means that it is possible to separate Ga(III) and Ge(IV) with combination nano-SiO_2 and nano-TiO_2.

The possible reasons of nano-SiO_2 adsorption gallium are as follows: gallium precipitates at pH 4–7.5. At a pH below 4, gallium exists in the form of Ga^{3+}, soluble complexes $Ga(OH)^{2+}$ and $Ga(OH)_2{}^+$. For a pH above 7.5, $Ga(OH)_4{}^-$ becomes predominant [23]. The surface charge of the nano-SiO_2 is neutral at isoelectric point (IEP) ($pH_{IEP} = 2.0$). The surface of sorbent carries positive charges at pH values lower than pH_{IEP}. At higher pH values (>pH_{IEP}), the surface of sorbent carries negative charges. Therefore, the effect of pH on Ga(III) adsorption can be explained by the following reasons: the surface of adsorbent carries negative charges at pH value higher than pH_{IEP} (pH > 2.0), which will enhances electrostatic force of attraction with Ga^{3+}, $Ga(OH)^{2+}$ and $Ga(OH)_2{}^+$. Therefore pH 3.5 was chosen for the adsorption Ga(III) to avoid the formation of insoluble $Ga(OH)_3$, which would affect the adsorption.

For germanium, when pH is below 2.0, Ge(IV) exists as Ge^{4+}. Within the pH range of 3.0–9.1, the primary aqueous Ge(IV) species include the neutral $Ge(OH)_4$. When pH ranges from 9.1 to 12.1, the primary aqueous Ge(IV) species include the negatively charged $GeO(OH)_3{}^-$. When pH is above 12.0, the primary aqueous Ge(IV) species is $GeO_3{}^{2-}$ [24]. Therefore, Ge(IV) cannot be adsorbed by nano-SiO_2 within the pH range of 1.0–13 pH range.

The possible reasons of nano-TiO_2 adsorption germanium are as follows: when pH below 4 or above 12, the electrostatic adsorption may play a major role on the adsorption of Ge(IV) on nano-TiO_2. The adsorption percentage of Ge(IV) decreased which may be mainly attributed to the formations of $\equiv TiOH_2{}^+$ and Ge^{4+} or $\equiv TiO^-$ and $GeO_3{}^{2-}$, the each couple of positive or negatively charge repels each other.

When pH ranges from 4.0 to 12.0, the mechanism of germanium species adsorbed on TiO_2 is complex. Besides electrostatic adsorption, adsorption of Ge(IV) may be through the formation of surface complexation reaction [25]:

$$\equiv \text{Ti–OH} + \text{Ge(OH)}_4 \rightleftharpoons \equiv \text{Ti–H}_n\text{GeO}_4^{(4-n-1)-} + \text{H}_2\text{O}(3-n)\text{H}^+$$

where $n = 0, 1, 2$.

In addition, aqueous Ge(IV) species adsorbed onto TiO_2 surface also may be through the formation of hydrogen bonds.

$$\equiv \text{TiOH}_2^+ + \text{Ge(OH)}_4^0 \rightleftharpoons \equiv \text{TiOH}_2\text{OHGe(OH)}_3^+$$

$$\equiv \text{TiOH}^0 + \text{Ge(OH)}_4^0 \rightleftharpoons \equiv \text{TiOHOHGe(OH)}_3$$

$$\equiv \text{TiO}^- + \text{Ge(OH)}_4^0 \rightleftharpoons \equiv \text{TiOHOHGe(OH)}_3^-$$

$$\equiv \text{TiO}^- + \text{Ge(OH)}_3^- \rightleftharpoons \equiv \text{TiOHOHGe(OH)}_2^{2-}$$

pH 4–12 was chosen for the sorption of Ge(IV) ions in the experiment.

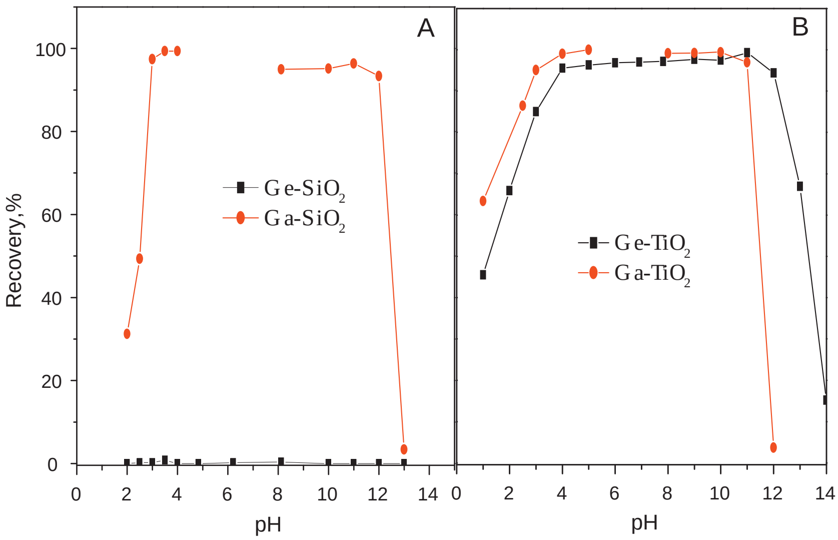

Fig. 1. Effects of pH on the adsorption of Ga(III)/Ge(IV) on sorbents, $C_{Ga(III)} = C_{Ga\ (III)} = 10\ \mu g\ mL^{-1}$, (A) nano-$SiO_2$ sorbents; (B) nano-TiO_2 sorbents.

3.2.2. *Effect of eluent concentration and volume*

The different concentrations of HNO_3 were studied for the elution of Ga(III) retained on nano-SiO_2. It was found that $1.0\ mol\ L^{-1}$ HNO_3 could quantitatively elute Ga(III) (>95%). The effect of the eluant volume on the recovery of Ga(III) was also investigated by keeping the HNO_3 concentration at $1.0\ mol\ L^{-1}$. The results showed that quantitative recoveries could be obtained with 1 mL of $1.0\ mol\ L^{-1}$ HNO_3. Moreover, in the same way, the recovery of Ge(IV) (>95%) was obtained with 2.0 mL of $K_3PO_4 + H_2SO_4$ mixture solution.

3.2.3. *The effect of sample volume on quantitative analysis using sorbents nano-SiO_2 and nano-TiO_2*

The effects of the sample volume on the recoveries of Ga(III) and Ge(IV) were studied. For this purpose, 10, 20, 30, 50, 75, 100 and 150 mL of sample solution volumes (containing 100 µg of Ge(IV)/Ga(III)) were adopted to test the effect of sample volume. It could be seen that the quantitative recoveries (over 95%) were obtained with a sample volume less than 20 mL for Ga(III) on nano-SiO_2 and 60 mL for Ge(IV) on nano-TiO_2. As described previously, 1 mL of $1.0\ mol\ L^{-1}$ HNO_3/2.0 mL of $K_3PO_4 + H_2SO_4$ was enough to elute the analytes adsorbed on sorbents, the enrichment factor of Ga(III)/Ge(IV) is about 20/30 [26].

3.2.4. *Sorption kinetic behaviors of Ga(III) and Ge(IV) onto sorbents*

In batch experiments, the Ga(III)/Ge(IV) ions sorption onto the nano-SiO_2/nano-TiO_2 sorbents was quite fast and the equilibrium was attained about 3 min (Fig. 2). For this reason 3 minutes was selected in all subsequent studies.

In order to investigate the adsorption processes of Ga(III) and Ge(IV) on the sorbents, pseudo-second-order kinetic models were used. The pseudo-second-order model is represented as [27]:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{3}$$

where q_e and q_t are the amount of target analytes adsorbed on the sorbent ($mg\ g^{-1}$) at equilibrium and at time t, respectively; k_2 is the rate constant of the second-order adsorption ($g\ mg^{-1}\ min^{-1}$). The straight-line plots of t/q_t versus t have been tested to obtain rate parameters.

The batch kinetic data were fitted to second-pseudo order model. The model adequately described the kinetic data at 95% confidence level. The results of the kinetic parameters for Ga(III) and Ge(IV) adsorption are listed in Table 2. Based on the correlation coefficients it follows that the adsorption of Ga(III) and Ge(IV) can be best described by the pseudo-second-order model ($R > 0.99$).

Furthermore, based on the rate constants given in Table 2, the activation energy (Ea) for the adsorption process can be calculated by employing the Arrhenius equation. The values of E_a for Ga(III) and Ge(IV) adsorption on sorbents were obtained to be 57.33 and $19.66\ kJ\ mol^{-1}$, respectively.

3.2.5. *Adsorption isotherms of Ga(III) and Ge(IV)*

Adsorption isotherms describe how solutes interact with the sorbents. In Fig. 3, the equilibrium adsorption amount of Ga(III) and Ge(IV) on the sorbents as a function of the equilibrium concentration of Ga(III) and Ge(IV) was depicted. An increased adsorption was observed for Ga(III) and Ge(IV) until saturation was attained.

Equilibrium sorption isotherms are often described by the Langmuir model [28]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b q_{max}} \tag{4}$$

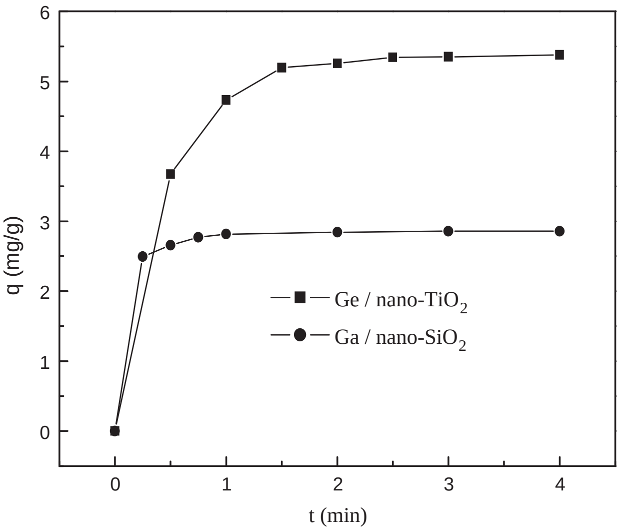

Fig. 2. Adsorption capacity of Ga(III) and Ge(IV) on sorbents versus time.

Table 2
The pseudo-second-order kinetic parameters for the target analytes adsorption on the different sorbents.

T (K)	Ga(III)/nano-SiO$_2$		R	Ge(IV)/nano-TiO$_2$		R
	k_2 (g mg^{-1} min^{-1})	q_2 (mg g^{-1})		k_2 (g mg^{-1} min^{-1})	q_2 (mg g^{-1})	
275	6.97	2.789	0.993	0.37	5.85	0.999
298	18.31	2.840	0.999	0.88	5.70	0.999
323	147	2.917	0.999	1.40	5.54	0.999

Data indicate that model parameters are statistically significant (t-test) at 95% confidence level.

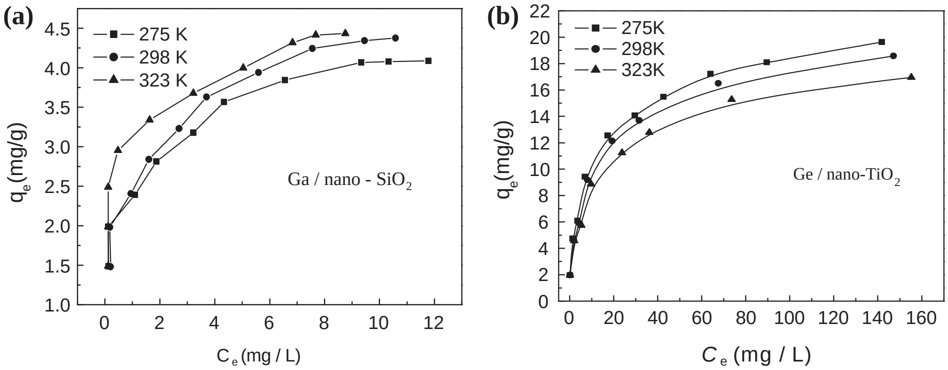

Fig. 3. Isotherm of Ga(III)/Ge(IV) adsorption on sorbents; 50 mg of sorbents; (a) the initial Ga(III) concentration range was 10–50 mg L^{-1}; (b) the initial Ge(IV) concentration range was 30–240 mg L^{-1}.

where $q_{\max}$ is the maximum monolayer adsorption (mg g^{-1}), and b is the Langmuir constant related to the affinity of binding sites (L mg^{-1}).

The Langmuir isothermal constants were determined from the plots of C_e/q_e against C_e, at 275 K, 298 K and 323 K, respectively. The obtained isothermal constants and the correlation coefficients are presented in Table 3. It was found that the adsorption of Ga(III)/Ge(IV) on sorbents correlated well ($R > 0.99$) with the Langmuir equation under the studied concentration range. The maximum adsorption capacity of Ga(III) and Ge(IV) ions on the nano-SiO$_2$ and nano-TiO$_2$ sorbents were 4.26 mg g^{-1} and 19.68 mg g^{-1} at room temperature, respectively.

3.2.6. Adsorption thermodynamic characteristics of Ga(III) and Ge(IV)

The sorption behaviors of different concentrations target analytes onto nano-SiO$_2$ and nano-TiO$_2$ sorbents were critically investigated at 275, 298, and 323 K, respectively. Gibbs free energy change (ΔG^0) of adsorption reaction at different temperatures can be calculated from following equation [29]:

$$\Delta G^0 = -RT \ \ln K_c \tag{5}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K) and K_c is the distribution coefficient. The K_c value was calculated using the following equation [29]:

$$K_c = \frac{q_e}{C_e} \tag{6}$$

The enthalpy change (ΔH^0) and entropy change (ΔS^0) of adsorption reaction were estimated from the following equation [29]:

$$\ln \ K_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{7}$$

According to Eq. (7), parameters, ΔH^0 and ΔS^0 parameters can be calculated from the slope and intercept of the plot of ln K_c versus $1/T$, respectively.

The values of ΔH^0, ΔS^0, and ΔG^0 for Ge(IV) and Ga(III) adsorptions were given in Table 4. The negative values of ΔH^0 and ΔG^0 showed the exothermic nature of the sorption process for Ge(IV), and the endothermic nature of adsorption process for Ga(III).

3.3. Effects of flow rates of sample and eluent solutions

The effect of sample solution flow rates on the adsorption of Ga(III) and Ge(IV) was examined under the optimum experimental conditions by passing a 10 mL of sample solution (containing 10 μg mL^{-1} Ga(III) or Ge(IV)) through the micro-column with the flow rate varying in the range of 0.3–2.0 mL min^{-1}. The results indicated that the quantitative recoveries (95%) of Ga(III) and Ge(IV) were obtained at flow rate lower than 0.5 mL min^{-1} through nano-SiO$_2$ and nano-TiO$_2$ micro-column, respectively. The recoveries of Ga(III) and Ge(IV) will decrease rapidly with increasing of the flow rate from 0.5 to 2.0 mL min^{-1}. Therefore, a flow rate of 0.5 mL min^{-1} is employed in this study.

The effect of eluent flow rates on the desorption of Ga(III) and Ge(IV) was also examined at the flow rate range of

Table 3
Langmuir constants of Ge(IV) and Ga(III) on the different sorbents.

T (K)	Ga(III)/nano-SiO$_2$		R	Ge(IV)/nano-TiO$_2$		R
	$q_{\max}$/mg g^{-1}	b/L mg^{-1}		$q_{\max}$ (mg g^{-1})	b (L mg^{-1})	
275	3.922	1.157	0.999	20.78	0.087	0.998
298	4.256	1.127	0.998	19.68	0.079	0.997
323	5.773	0.824	0.998	17.58	0.073	0.997

Data indicate that model parameters are statistically significant (t-test) at 95% confidence level.

Table 4
Thermodynamic parameters for the adsorption of the target analytes on the different sorbents.

Analyte/sorbents	C_0 (mg mL^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	ΔG^0 (kJ mol^{-1})			R
				275 K	293 K	313 K	
Ga(III)/nano-SiO$_2$	4.0×10^{-2}	6.18	97	−20.63	−22.39	−24.34	0.999
	4.5×10^{-2}	5.69	93	−19.86	−21.53	−23.39	0.993
	5.0×10^{-2}	8.72	102	−19.20	−21.02	−23.05	0.991
Ge(IV)/nano-TiO$_2$	3.4×10^{-2}	−6.86	−51	−6.85	−6.85	−6.84	0.996
	12×10^{-2}	−5.81	−60	−5.79	−5.79	−5.79	0.993
	18×10^{-2}	−4.60	−61	−4.58	−4.58	−4.58	0.995

Data indicate that model parameters are statistically significant (*t*-test) at 95% confidence level.

0.3–2.0 mL min^{-1} with 1.0 mL of 1.0 mol L^{-1} HNO_3 for Ga(III) and 2.0 mL of $K_3PO_4 + H_2SO_4$ for Ge(IV). It was found that the recoveries of Ga(III) and Ge(IV) strongly depended on the eluent flow rate, the higher the flow rate of the solution, the lower the recoveries of Ga(III) and Ge(IV). When the flow rate was controlled within the range of 0.3–1.0 mL min^{-1}, the recoveries of Ga(III) and Ge(IV) were over 95%. Therefore, the eluent flow rate of 1.0 mL min^{-1} was selected in this work.

3.4. Adsorption capacity

Under the optimal conditions, the determination of dynamic adsorption capacity was performed. A 10 mL of sample solution (10 μg mL^{-1} Ga(III) or Ge(IV)) was adjusted to the appropriate pH and passed through the micro-column with a flow rate of 0.5 mL min^{-1}. Each 10 mL of effluent solution was collected for the determination of Ga(III) or Ge(IV) concentration until Ga(III)/Ge(IV) concentration equates the initial concentration. Breakthrough curve were obtained by plotting C/C_0 versus effluent volume, and the results were shown in Fig. 4. The adsorption capacity evaluated from the breakthrough curve is 4.6 for Ga(III), and 20.1 mg g^{-1} for Ge(IV).

3.5. Interference study

The effects of common coexisting cations and anions on the separation of both Ga(III) on nano-SiO_2 and Ge(IV) on nano-TiO_2 were examined. Solutions of 20 μg mL^{-1} Ga(III) and Ge(IV) containing the added interfering ions were treated according to the recommended procedure. The tolerance of the coexisting ions is defined as the largest amount making the recovery of the studied elements less than 95%. The experimental results indicated that 1000 mg L^{-1} K^+, 1000 mg L^{-1} Na^+, 700 mg L^{-1} Ca^{2+}, 700 mg L^{-1} Mg^{2+}, 50 mg L^{-1} Zn^{2+}, 50 mg L^{-1} V^{5+}, 5 mg L^{-1} Fe^{3+}, 5 mg L^{-1} Al^{3+}, 5 mg L^{-1} Mn^{2+}, 5 mg L^{-1} Sn^{4+}, 5 mg L^{-1} Si^{4+}, 20 mg L^{-1} Cu^{2+}, 20 mg L^{-1} Cd^{2+}, 20 mg L^{-1} Co^{2+}, 20 mg L^{-1} Ni^{2+}, 1800 mg L^{-1} $SO_4{}^{2-}$, 900 mg L^{-1} $NO_3{}^-$, 250 mg L^{-1} $PO_4{}^{3-}$, 1000 mg L^{-1} Cl^- had no obvious influence on the separation and determination of Ga(III) and Ge(IV) under the recommended conditions, and the most serious interference arose from Si (IV) Sn(IV), Al(III) and Fe(III). But they can be completely eliminated in the process of dissolving ores samples. Sn(IV) can form highly volatile $SnBr_4$ during the sample preparation process. Si (IV) can form silicic acid, and silicic acid can be dehydrated to form insoluble residue SiO_2 by adding hydrochloric acid and sulfuric acid (twice evaporate the solution to near dryness), respectively. Al(III) and Fe(III) can also be eliminated, because HF was be used during the sample preparation process.

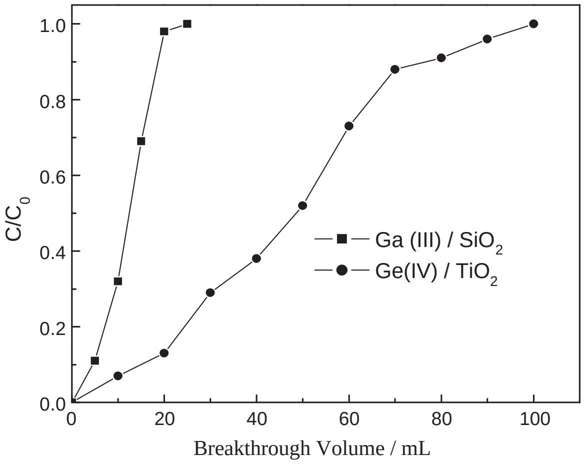

Fig. 4. Breakthrough curve of Ga(III)/Ge(IV) on the nano-SiO_2/TiO_2 column.

Table 5
Determination of Ga and Ge in certified reference materials (mean ± SD., $n = 7$).

Samples	Species	Certified (μg g^{-1})	Found (μg g^{-1})
GBW 07406	Ga(III)	30 ± 4	29 ± 2
	Ge(IV)	3.2 ± 0.4	3.0 ± 1.9
GBW 07311	Ga(III)	26 ± 4	27 ± 2
	Ge(IV)	3.1 ± 0.4	2.9 ± 0.6

3.6. Detection limits and precision

Under the optimum conditions described above, the calibration graphs for Ga(III) and Ga(III) were linear in the range 0–10 μg/25 mL and 0–6 μg/25 mL, the calibration equations is $C_{Ga} = 0.9013A + 0.1013$ ($r = 0.9993$, $\varepsilon = 0.65 \times 10^5$ L mol^{-1} cm^{-1}) and $C_{Ge} = 0.3837A - 0.0266$ ($r = 0.9994$, $\varepsilon = 1.55 \times 10^5$ L mol^{-1} cm^{-1}), respectively. Where C is the concentration of target analytes (μg/25 mL), and A is the absorbance. The detection limits for Ga and Ge with enrichment factors of 20 and 30 were found to be 4.5 and 7.2 ng mL^{-1}, and the relative standard deviations (R.S.D., $n = 11$, $C = 10$ μg mL^{-1}) were 3.9 and 2.2%, respectively.

3.7. Analytical application

In order to verify the validity of the proposed method, it was applied to the determination of the content of gallium and germanium in standard reference materials according to the recommended procedure. The analytical results were listed in Table 5. As good agreement between the determined values and the certified or reference values have been obtained.

Table 6
Recoveries of Ga(III) or Ge(IV) in mixed standard solution and spiked waste water sample (mean ± SD., $n = 7$).

Samples	Spike (μg mL^{-1})		Recovery (%)	
	Ge(IV)	Ga(III)	Ge(IV)	Ga(III)
Synthetic-1	0.4	1	93.4	92.4
Synthetic-2	3	2	97.2	99.4
Synthetic-3	6	5	103.9	95.7
Industrial waste water	–	–	Not detected	Not detected
	5	5	99.4	97.6
	10	10	96.9	105.0

The method was also applied to the determination of gallium and germanium in the industrial waste water and synthetic samples, and the analytical results were presented in Table 6. The recoveries were found to be in the range of 96.4–105.0%.

4. Conclusion

In this paper, the adsorption behaviors of Ga(III) and Ge(IV) ions on nano-SiO_2 and nano-TiO_2 was investigated. Kinetic studies suggest that the equilibrium could be achieved within 3 min and a pseudo-second-order is followed. The adsorption isotherms could be well fitted applying the Langmuir. The thermodynamic data confirmed the endothermic nature of Ga(III) sorption onto nano-SiO_2, and the exothermic nature of Ge(IV) sorption onto nano-TiO_2. The experimental results indicate that nano-SiO_2 is an efficient adsorption material for the simultaneous speciation of inorganic gallium and germanium. The combination of nano-SiO_2 and TiO_2 packed columns provides a simple, reliable, fairly rapid and low cost method which has been successfully used for the separation and preconcentration of Ga(III) and Ge(IV) from the geological samples with a complex matrix.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.07.096.

References

[1] I. Mihaylov, P.A. Distin, Hydrometallurgy 28 (1992) 3–27.
[2] X. Querol, J.L. Fernandez-Tutiel, A. Lopez-Soler, Fuel 74 (1995) 331–343.
[3] O. Font, X. Querol, R. Juan, R. Casado, R.C. Ruiz, A. Lopez-Soler, P. Coca, F. Garcia Pena, J. Hazard. Mater. A139 (2007) 413–423.
[4] A. Hernandez-Exposito, J.M. Chimenos, A.I. Fernandez, O. Font, X. Querol, P. Coca, F. Garcia Pena, Chem. Eng. J 118 (2006) 69–75.
[5] D. Kalderis, E. Tsolaki, C. Antoniou, E. Diamadopoulos, Desalination 230 (2008) 162–174.
[6] J.O. Esalah, M.E. Weber, J.H. Vera, Can. J. Chem. Eng. 78 (2000) 948–954.
[7] E. Rodil, R. Dumortier, J.H. Vera, Chem. Eng. J. 97 (2004) 225–232.
[8] B.Y. Mishra, M.D. Rokade, P.M. Dhadke, Indian J. Chem. 39 (2000) 1114–1116.
[9] B. Gupta, N. Mudhar, I. Singh, Sep. Purif. Technol. 57 (2007) 294–303.
[10] M.S. Lee, J.G. Ahn, E.C. Lee, Hydrometallurgy 63 (2002) 269–276.
[11] O. Font, X. Querol, A. Lopez-Soler, J.M. Chimenos, A.I. Fernandez, S. Burgos, F. Garcia Pena, Fuel 84 (2006) 1384.
[12] O. Font, X. Querol, A. López-Soler, J.M. Chimenos, Fuel 84 (2005) 1384–1392.
[13] Z. Klika, L.I. Ambruzová, Sýkorová, Fuel 88 (2009) 1834–1841.
[14] J.P. Marco-Lozar, D. Cazorla-Amoro, A. Linares-Solano, Carbon 45 (2007) 2519–2528.
[15] Y. Inukai, Y. Tanaka, Y. Shiraishi, Anal. Sci. 17 (2001) i1117–i1120.
[16] G. Gokturk, M. Delzendeh, M. Volkan, Spectrochim. Acta B 55 (2000) 1063–1071.
[17] H.L. Zhao, J. Liu, Chin. J. Rock Miner Anal. 29 (2010) 465–468.
[18] L. Zhang, Y. Zhu, H.M. Li, Rare Met. 29 (2010) 16–19.
[19] L. Zhang, T. Huang, N. Liu, X.Y. Liu, H.M. Li, Microchim. Acta 165 (2009) 73–78.
[20] F. Lin, M.X. Huang, J. Anal. Sci. 13 (1997) 157–159.
[21] H.X. Shen, Z.Q. Wang, China Academic Journal Electronic Publishing House (1994–2006), pp. 8–11.
[22] V.C. Srivastava, I.D. Mall, I.M. Mishra, Chem. Eng. J. 132 (2007) 267–278.
[23] R. Dumortier, E. Martin Weber, H. Juan Vera, Hydrometallurgy 76 (2005) 207–215.
[24] Y. Inukai, Y. Kaida, S. Yasuda, Anal. Sci. 13 (1997) 221–224.
[25] L. Zhang, H.M. Li, G.X. Han, Chem. J. Chin. Univ. 31 (2009) 130–140.
[26] A. Mizuike, Enrichment Techniques for Inorganic Traces Analysis, Springer-Verlag, Berlin, New York, 1983, pp. 6–8.
[27] Y.S. Ho, G. McKay, Process Biochem. 34 (1999) 451–465.
[28] I. Langmuir, J. Am. Chem. Soc. 40 (1918) 1361–1403.
[29] G. Bereket, A.Z. Aroğuz, M.Z. Özel, J. Colloid Interface Sci. 187 (1997) 338–343.