

# Spectrophotometric quantification of germanium (IV) in environmental samples using chemically modified chitosan sorbent and optimized cloud phase extraction method.

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## Abstract

Biopolymers as chitosan which is one of the emerging sorption material for the removal of metal ions was applied to determine germanium(IV), even at low concentrations. A selective, sensitive and rapid method was described for preconcentrative determination of Ge(IV) using the synthesized 2-amino-4-(m-tolyazo)pyridine-3-ol (ATAP), which was chemically immobilized on chitosan. The sorbent synthesized material was selective to Ge(IV) within a best response time of 10 min. The procedure was selective in presence of other diverse anions and cations. Under the optimum experimental conditions, calibration plots were linear over the concentration range of 2.5 to 75 ng mL<sup>-1</sup> of Ge(IV). The obtained results are 100 times lower than by the direct determination of Ge(IV) by FAAS. The developed method is repeatable with a relative standard deviation of 2.55%. The developed sorbent was applied successfully to determine Ge(IV) in environmental samples. Unlike most preconcentration methods, the present enrichment work allowed for a rapid and reliable determination of Ge(IV) in real water and soil samples by the simple, rapid and routinely available spectrophotometric technique.

**Keywords:** Germanium (IV) determination, Chitosan, Preconcentration, Spectrophotometry, Environmental samples

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## Introduction

Germanium is present in nature dispersed in ore deposits, mainly as soluble methylgermanium species and germanate anions [1,2]. It is an element widely used in, e.g., as a catalyst in production of plastics or semiconductor production [3]. Germanium determination and its concentration on ultra-trace levels has been pursued for many years [3,4]. Enrichment (also named preconcentration) is a generic term for different processes employed to increase the level of a desired element to be suitable for further processing, e.g., its determination, increases the sensitivity by several orders of magnitude, facilitates calibration, preconcentration improves the analytical detection limit, and enhances the accuracy of the results. Some preconcentration procedures, e.g., sorption [5–10], liquid-liquid extraction [11–15], coprecipitation [16,17], and cloud point method [18], is employed in combination with spectroscopic and spectrophotometric detection methods [11,19–33] to determine Ge(IV) ions. The germanium preconcentration by sorption offers various advantages over other methods of concentration (e.g., liquid-liquid extraction), such as experimental convenience, usage of less toxic materials and low cost. To date, there are a few studies related to preconcentration Ge(IV) ions on a solid substrate, for instance on Kelex-100 [11], nanometer sized TiO<sub>2</sub>/SiO<sub>2</sub> [3], TiO<sub>2</sub> [2,19], active carbon [34], cellulose [9], chitosan chelating resin [5,9,11], Sephadex gel [6], anionic resin (IRA-900) [31], goethite [34] and mercapto modified silica gel [8]. Therefore, the described sorbents have one or more of the following disadvantages: low rate of sorption [3,27,29], relatively low selectivity, low sorption capacity [34],

or high cost of sorbent [7,34,35]. A new inexpensive sorbent with best analytical parameters for at least some of the above mentioned points constitutes an important task.

Several analytical reagents have already been applied for the spectrophotometric determination of Ge(IV) [11,19–33], whereas, the analytical parameters for them are rather moderate. In fact, none of the reagents described have good integrate analytical parameters (large scale for determination, low detection limits, low cost and selectivity). Therefore, introduce a new effective reagent; 2-amino-4-(m-tolyazo)pyridine-3-ol (ATAP), for easy and straight forward determination of Ge(VI) was decided.

Recently, to treat low concentration of heavy metals from environmental samples chitosan was used due to its high adsorptive capacity when compared to other adsorbents [25,26]. In this study, a rapid selective and sensitive procedure is investigated to preconcentrative determination of Ge(IV) applying the synthesized 2-amino-4-(m-tolyazo)pyridine-3-ol (ATAP), which was chemically immobilized on chitosan. Therefore, the goal of this study is to develop a new routine procedure for the effective preconcentration of Ge(IV) combined with its spectrophotometric determination.

## Methodology

### Apparatus

Atomic absorption spectrometer model 6300 (AAS), Shimadzu (Japan), was used for measurements with flame of N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> and the instrument settings were adjusted according to the

manufacturer's recommendations. IR spectrometer (Thermo-Nicolet FT-IR, Nicolet IR-200, USA) was used for the analysis of functional groups in the synthesized reagent. An Orion research model 601 A/digital ionalyzer pH meter was used for checking the pH of solutions. A Perkin-Elmer Lambda 12 UV/Vis spectrometer was used for recording absorbance spectra with 5.0 mm quartz cell. A centrifuge with 25-mL calibrated centrifuge tubes (Superior, Germany) was used to accelerate the phase separation process.

### **Special chemical preparations**

All the reagents used in this work were of analytical grade and all solutions were prepared in polypropylene volumetric flasks. A  $1.00 \times 10^{-2}$  M solution of Ge(IV) was prepared by dissolving metallic germanium (99.99%) as described [36] and Ge(IV) concentration was determined by atomic absorption spectroscopy [37]. The stock solutions of the various metal ions ( $\text{mg L}^{-1}$ ) were prepared with their nitrate or chloride salts ( $\geq 99.99\%$ ) and used to illustrate the possible effects of interfering ions. Doubly distilled water was used throughout the experiments.

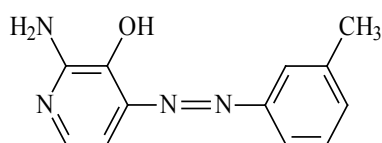
Solutions of alkali metal salts (1.0%) and various metal salts (0.1%) (Sigma, St Louis, MO, USA) were used to study the interference of anions and cations, respectively. Acetate buffer solutions ( $\text{HOAc-NH}_4\text{OAc}$  buffer) of pH 2.75–5.61 were prepared as recommended [38].

### **Synthesis of 2-amino-4-(m-tolyazo)pyridine-3-ol**

2-Amino-4-(m-tolyazo)pyridine-3-ol (ATAP) (Figure 1) was prepared according to way used for preparing azo dye derivative of aromatic amine. 0.01 mole of m-toluidene was converted to the hydrochloric form by adding the least amount of 1:1 HCl then diluting with water and cooling at  $-2.0^\circ\text{C}$ . A cooled solution of  $\text{NaNO}_2$  (0.01 mole) was added gradually with continuous stirring to the amine salt. The resulting diazonium salt solution was allowed to stand in ice bath for 15 min with stirring at  $-2.0^\circ\text{C}$  and then added gradually to a solution of 0.01 mole of 2-amino-3-hydroxypyridine dissolved in 10% NaOH which cooled at  $-2.0^\circ\text{C}$ . The resulting solution was allowed to stand for 15 min with constant stirring until the azo dye completely formed. The obtained azo was filtered off, dried and recrystallized in ethanol. The purity of the resulting azo dye was checked by measuring the melting point constancy. The chemical structure was detected by melting point, elemental analysis (C, H, N), IR and  $^1\text{H-NMR}$  spectra. The separated azo has the following structural formula: A  $5 \times 10^{-3}$  M solution of the reagent was prepared by dissolving an appropriate amount of reagent in 10 mL ethanol and completed to the mark in 100 mL calibrated flask.

### **General procedure**

To determine concentration of Ge(VI), standard solutions were adjusted to  $\text{pH}=3.5 \pm 0.1$  by adding 3.0 mL of acetic acid acetate



**Figure 1.** 2-amino-4-(m-tolyazo)pyridine-3-ol (ATAP).

buffer. 0.8 mL of  $5 \times 10^{-3}$  M ATAP solution, and 3.0 mL of 5.0% Triton X-100 solution (Sigma, St Louis, MO, USA) was added and allowed to stand for 5.0 min at room temperature. Then 3.0 mL of 0.3 M KCl solution was added. An amount of 40 mg of chitosan was added to the above solution and the mixture was shaken for 5.0 min and made up to the mark in 25 mL measuring flask with doubly distilled water. Separation was accelerated by centrifugation for 5.0 min at 3800 rpm, then the aqueous phase could be isolated by overturning the tube. The surfactant-rich phase was dissolved in 0.1 mL of acetonitrile, and transferred into a 5.0 mm quartz cell. The absorbance of the solution was measured at 547 nm against a blank solution prepared in the same way but without Ge(IV) ions.

### **Procedure for soil analysis**

Soil samples were collected from industrial sites of Shoubra and Quesna cities. The soil samples were collected and air dried at  $70^\circ\text{C}$  in the laboratory oven and then grinded to fine powder and sieved through 0.25 mm nylon mesh. A 10 mL concentrated HCl and 3.0 mL concentrated  $\text{HNO}_3$  were added to one gram of soil sample, and kept for overnight [39]. After digestion and filtration, the solution was subjected to separation by following the general procedure described above.

### **Application to real samples**

The developed method was applied to quantify Ge(IV) ions in the real water and soil samples collected in and around industrial sites of Shoubra and Quesna. The general procedure described above was applied to 20 mL of water sample (tap water/ground water) and acid digested soil sample was followed.

### **Interference study**

The interference of foreign ions like  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  was studied by equilibrating the fixed amount of  $\text{Ge}^{4+}$  along with the reagent sorbent solution at  $\text{pH}=3.5$  and later the determinations was made using the general procedure described above.

## **Results and Discussion**

### **Reaction conditions**

The reaction conditions were investigated with  $40 \text{ ng mL}^{-1}$  solution of Ge(IV). Sorption was carried out in different buffer media, and other variables were kept constant. It was found that Ge-complex was quantitatively sorbed on chitosan in an acetate buffer solution of pH 3.5. Addition of 2.5–3.5 mL of a pH 3.5 solution did not affect the CPE of Ge-complex and the use of 3.0 mL is recommended.

The effects of surfactants on the Ge-ATAP system were studied. The results indicated that, in the presence of anionic or cationic surfactants, the Ge-ATAP chromogenic system gives a low absorption, whereas in the presence of nonionic surfactants, the absorption of the chromogenic system increases markedly. Various nonionic surfactants enhance the absorbance in the following sequence:

Triton X-100 > Triton X-114 > Tween-20 > Tween-60 > Tween-80 > emulsifier-OP

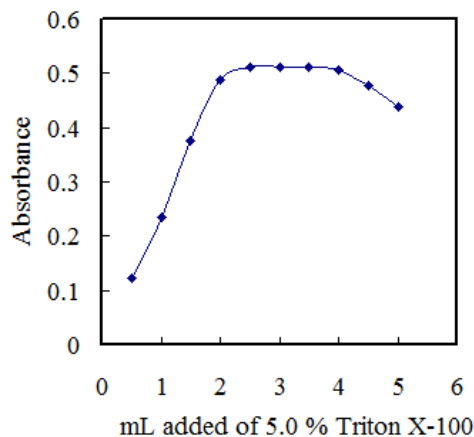
The Triton X-100 was the optimum one, and the use of 2.5–

3.5 mL of 5.0% Triton X-100 solution gave a constant and maximum absorbance value (Figure 2). Consequently, the use of 3.0 mL was recommended.

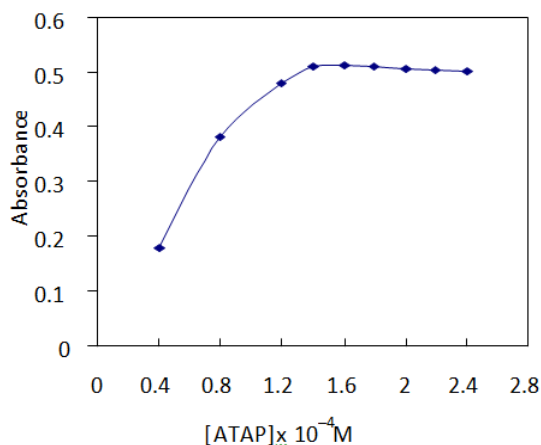
For up to 40 ng of Ge(IV), The effect of ATAP concentration on the extraction and quantification of Ge(IV) was illustrated in the range of (0.2–1.4 mL) of  $5 \times 10^{-3}$  M. The sensitivity of the procedure was increased by increasing the ATAP concentration up to  $1.4 \times 10^{-4}$  M and remained constant at higher concentrations. Therefore,  $1.6 \times 10^{-4}$  M ATAP was applied in all further work. The results are represented in Figure 3. The slight decrease in absorbance after  $1.6 \times 10^{-4}$  M ATAP by about 3.0% is likely to be due to the concentration of uncomplexed ATAP in the surfactant rich phase being increased significantly, so free ATAP competes with the complexes for extraction to the surfactant rich phase.

The volume of the aqueous phase was changed in the range of 2.0–100 mL under the optimum experimental conditions, keeping the other variables constant. It was observed that the highest absorbance value was almost constant up to 25 mL. However, for convenience, all the experiments were carried out with 25 mL of the aqueous phase.

Addition of salts can cause cationic surfactant solutions to separate into two phases: immiscible surfactant-rich and surfactant-poor phases. Therefore, different concentrations



**Figure 2.** Effect of 5.0 % Triton X-100 on the complexation of 40 ng mL<sup>-1</sup> Ge(IV) using ATAP at the optimum condition.



**Figure 3.** Effect of ATAP concentration on the absorbance of 40 ng mL<sup>-1</sup> Ge(IV) at the optimum conditions.

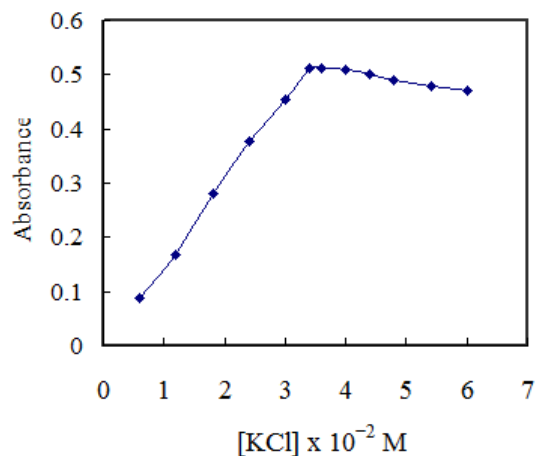
of potassium chloride were added to prompt micellar growth and extraction of the formed complex. The effect of chloride concentration was investigated in the range of (0.5–5.0 mL) of 0.3 M. The results indicated that addition of  $3.4 \times 10^{-2}$  M chloride was sufficiently for maximum extraction of the complex and the absorbance remained constant at higher concentrations, as exhibited in Figure 4.

A concentration of  $3.6 \times 10^{-2}$  M chloride was selected for further work. The effect of time on the reaction and also on the CPE procedure was investigated. The results showed that the complex formation of Ge–ATAP was completed in 5.0 min, and 5.0 min centrifugation at 3800 rpm was found to be enough for complete CPE.

The sensitivity and selectivity can be increased by sorbed the formed complex on biopolymer chitosan. Chemically modified chitosan sorbent would be modified the method to be more sensitive and selective. Different weight of chitosan sorbent was tested ranging from 10 to 70 mg. A 40 mg of chitosan gave the highest absorbance value in addition to smallest volume of acetonitrile is used for CPE. Without chitosan, CPE take 2.5 mL of acetonitrile with half absorbance value obtained on using chitosan sorbent, whereas 0.1 mL of acetonitrile was sufficient to dissolve the surfactant-rich phase. Hence using 40 mg chitosan was sufficient for the effective preconcentration. Therefore, a preconcentration factor of 250 was archived using chitosan, whereas it reach 10 only without chitosan.

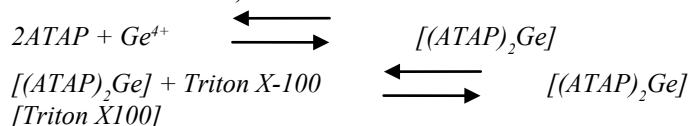
#### Stoichiometric ratio

The nature of the complex was illustrated at the optimum experimental conditions described above using the molar ratio and continuous variation methods. The plot of absorbance versus the molar ratio of ATAP to Ge(IV), obtained by varying the ATAP concentration, showed inflection at a molar ratio of 2.0, indicating the presence of two ATAP molecules in the formed complex. Moreover, the Job method showed a ratio of ATAP to Ge(IV)=2.0. Consequently, the results indicated that the stoichiometric ratio was (2 : 1) [ATAP : Ge]. For the ternary complex with Triton X-100, the obtained results implied that a 1 : 1 complex is formed between the [(ATAP)<sub>2</sub>Ge] complex and Triton X-100. Consequently, the results indicated that the



**Figure 4.** Effect of KCL concentration on the completion of 40 ng mL<sup>-1</sup> Ge (IV) at the optimum.

stoichiometric ratio was 2 : 1 : 1 [(ATAP)<sub>2</sub>Ge][Triton X-100], as shown in the following equations. Using Harvey and Manning equation applying the data obtained from the above two methods, the calculated conditional formation constant (log K), was found to be 3.87, whereas the true constant was 3.65.



### Stability of the chromogenic system

The absorbance reaches its maximum simultaneously at room temperature after mixing the components, and remains stable for 3.0 h in aqueous solution. After extracted into acetonitrile, the complex was stable for at least 12 h.

### Effect of foreign ions

The effect of the interfering species upon the sorption was investigated using the proposed procedure at optimized conditions applying 40 ng of Ge(IV). The tolerance limit was set as the concentration of the diverse ion required to cause  $\pm 5.0\%$  error in the determination of Ge(IV). The tolerance limit (error < 5.0%) is recorded in Table 1. The results showed that alkaline and earth-alkaline metals, Mn<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Pb<sup>2+</sup>, In<sup>3+</sup>, Bi<sup>3+</sup>, Al<sup>3+</sup>, Ga<sup>3+</sup>, Sn<sup>4+</sup>, Zr<sup>4+</sup>, Ti<sup>4+</sup>, and Hf<sup>4+</sup>, as well as anions had no significant effect on the separation and determination of Ge(IV) under the recommended experimental conditions, and the most serious interference arose from Cu<sup>2+</sup> and Fe<sup>3+</sup> (Table 1). However, the interference can be completely eliminated by masking with 0.5 mL of 0.01 M oxalic acid or citric acid. The above results also clearly demonstrate that the described herein sorbents show much better selectivity for the Ge(IV) ion

**Table 1.** Separation of Ge(IV) in the presence of different diverse ions.

Ion	Added as	Concentration ( $\mu\text{g mL}^{-1}$ )	Recovery (%) Ge(IV)
Na <sup>+</sup>	NaCl	17000	98.2
K <sup>+</sup>	KCl	14000	97.5
Mg <sup>2+</sup>	MgCl <sub>2</sub>	12000	98.2
Ca <sup>2+</sup>	CaCl <sub>2</sub>	10000	98.9
Ba <sup>2+</sup>	BaCO <sub>3</sub>	8500	97
Mn <sup>2+</sup>	Mn(NO <sub>3</sub> ) <sub>2</sub>	6500	96.8
Cd <sup>2+</sup>	Cd(NO <sub>3</sub> ) <sub>2</sub>	3500	96.7
Ni <sup>2+</sup>	Ni(NO <sub>3</sub> ) <sub>2</sub>	2500	96.8
Zn <sup>2+</sup>	Zn(NO <sub>3</sub> ) <sub>2</sub>	1750	96.5
Co <sup>2+</sup>	Co(NO <sub>3</sub> ) <sub>2</sub>	1400	96.2
Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	1000	97.6
Hg <sup>2+</sup>	HgCl <sub>2</sub>	750	99
Ag <sup>+</sup>	AgNO <sub>3</sub>	600	98.5
Ti <sup>4+</sup>	Ti(SO <sub>4</sub> ) <sub>2</sub>	500	98.6
Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	400	99.5
Al <sup>3+</sup>	Al(NO <sub>3</sub> ) <sub>3</sub>	300	98.3
In <sup>3+</sup>	In(NO <sub>3</sub> ) <sub>3</sub>	250	96.5
Ga <sup>3+</sup>	Ga(NO <sub>3</sub> ) <sub>3</sub>	225	94.2
Sn <sup>4+</sup>	Sn(SO <sub>4</sub> ) <sub>2</sub>	200	97.3
Zr <sup>4+</sup>	Zr(SO <sub>4</sub> ) <sub>2</sub>	175	95.9
Hf <sup>4+</sup>	Hf(SO <sub>4</sub> ) <sub>2</sub>	150	96.5
Bi <sup>3+</sup>	Bi(NO <sub>3</sub> ) <sub>3</sub>	100	97.8
Cu <sup>2+</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub>	50	97.2
Fe <sup>3+</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub>	25	96.2

Note: \* masked with 0.5 mL of 0.01 M oxalic or citric acid

in comparison to the previously described ones, especially in view of such interfering ions as Co<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Sn<sup>4+</sup> and PO<sub>4</sub><sup>3-</sup> [2,3,29,30].

### Calibration curve and sensitivity

The calibration curve indicated that the system obeys Beer's law in the concentration range of 0.5–75 ng Ge(IV) per mL in the measured solution. For more accurate results, the Ringbom optimum concentration range was found to be 2.0–70 ng Ge(IV) per mL in the measured solution. These values are 100 times lower than by the direct determination of germanium by AAS. The linear regression equation obtained was  $A=12.8C$  ( $\mu\text{g mL}^{-1}$ ) + 0.0053 ( $r=0.9992$ ). The molar absorptivity was calculated to be  $9.30 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 547 nm, whereas the Sandell sensitivity was found to be 0.078 ng cm<sup>-2</sup> (Table 2). The standard deviations of the absorbance measurements were calculated from a series of 13 blank solutions. The limits of detection (K=3) and of quantification (K=10) of the method were established [40] and recorded in Table 2, according to the IUPAC definitions ( $C_1=KS_0/s$  where  $C_1$  is the limit of detection,  $S_0$  is the standard error of blank,  $s$  is the slope of the standard curve and  $K$  is the constant related to the confidence interval). The relative standard deviation was 2.25% obtained from a series of 10 standards each containing 40 ng mL<sup>-1</sup> of Ge (IV).

Because the amount of Ge (IV) in 25 mL of the sample solution was measured, and after preconcentration by CPE the final volume is 2.5 mL, the maximum preconcentration factor of the solution is 10. On using modified sorbent chitosan, the preconcentration factor is increase to 250. The improvement factor, defined as the ratio of the slope of the calibration graph for the CPE method without and with chitosan to that of the calibration graph in aqueous media (before applying the CPE method), for Ge(IV) was 12.5 and 450, respectively.

A comparison of the proposed procedure with the previously reported procedures for preconcentration and spectrophotometric determination of Ge(IV)<sup>9-33</sup> (Table 3) indicates that the proposed procedure is faster and simpler

**Table 2.** Analytical features of the proposed method.

Parameters	CPE without chitosan	Using chitosan
Amount of acetonitrile	2.5	0.1
pH	3.5	3.5
Optimum [ATAP] M	$1.6 \times 10^{-4}$	$1.6 \times 10^{-4}$
Reaction time (min)	20	5
Stirring time (min)	10	5
Beer's range (ng mL <sup>-1</sup> )	500 - 8500	0.5 - 75
Ringbom range (ng mL <sup>-1</sup> )	1000 - 8000	2.0- 70
Molar absorptivity (L mol <sup>-1</sup> cm <sup>-1</sup> )	$2.28 \times 10^4$	$9.30 \times 10^5$
Sandell sensitivity (ng cm <sup>-2</sup> )	25.2	0.078
Regression equation		
Slope ( $\mu\text{g mL}^{-1}$ )	0.314	12.8
Intercept	-0.014	0.05
Correlation coefficient (r)	0.9976	0.9992
RSD a (%)	3.1	2.25
Detection limits (ng mL)	130	0.17
Quantification limits (ng mL <sup>-1</sup> )	440	0.5
enhancement factor	10	250
Improvement factor	12.5	450

**Table 3.** Survey of spectrometric methods applied for the determination of germanium.

Spectrophotometric reagent	LOD $\mu\text{g mL}^{-1}$	Beer's law $\mu\text{g mL}^{-1}$	Selectivity	Analyzed sample	Ref.
<i>o</i> -Chlorophenylfluorone <sup>a</sup>	0.0– 12	125	Ni(II), Co(II), Sn(II), Fe(II), Zn(II), Mn(II), Pt(IV), Cr(III), W(III), Al(III), V(V), Ti(IV), La(III), Au(III), In(III), Mo(IV), Zr(IV), Sb(III), Ag(I),	Water	[19]
9-( <i>o</i> -Chlorophenyl)-2,6,7-trihydroxyxanthen-3-one in the presence of cetyltrimethylammonium bromide <sup>a</sup>	0.0– 200		Ba(II), Pb(II), Ga(III), Sb(III), V(V), Cr(VI), W(VI), Mo(VI)	Minerals and Ores	[20]
polysulfone membrane filter- Ge(IV)-9-phenyl-3-fluorone complex	2.1	Up to 7.0	Al(III), Fe(III), Si(IV), Sn(IV),	soil and water	[21]
Phenylfluorone and zephiramine <sup>a</sup>	0 – 0.10	47.5	Sb(III), Sn(II, IV), W(VI), Mo(VI), Ta(V), Nb(V)	Hot spring water and ground water	[7]
Nano-sized TiO <sub>2</sub> <sup>c</sup>	43		Sr(II), Zn(II), PO <sub>4</sub> <sup>3-</sup> , F <sup>-</sup>	Water	[3]
Catechol violet and cetyltrimethylammonium bromide <sup>a</sup>	0.1 – 1.0		Sb(III), Fe(III), Bi(III), Sn(IV), V(V), Cr(VI), Mo(VI),		
<i>o</i> -sulfofenylfluorone (SPF) and cetyltrimethylammonium chloride (CTAC).	0.0026	0.007-0.40	Sb(III), Sb(V), Sn(II), Sn(IV), Mo(VI), Ti(IV)	human urine	[22]
Precipitation with Fe(OH) <sub>3</sub> and determination with trimethoxyphenylfluorone <sup>a</sup>	0 – 0.24	21	Sr(II), Pb(II), Zr(IV), Ti(IV), Mo(VI)	Foods	[23]
Preconcentration on an organic solvent-soluble membrane and determination with <i>o</i> -nitrophenylfluorone in presence of sodium dodecyl sulfate <sup>a</sup>	0.02 – 0.36	0.0– 40	Pb(II), Mo(VI)	Chinese herb, Natural-, drinking-waters, urine sample	[15]
Nano-TiO <sub>2</sub> (salicyl fluorone in the presence of cetyltrimethylammonium bromide) <sup>a</sup>	0 – 0.24	0.072	Al(III), Fe(III), Si(IV), Sn(IV),	Water and certified reference material (GBW07311)	[2]
Preconcentration/separation procedure (spectrophotometric reagent) Pyrogallol <sup>b</sup>	0 – 18	12 × 90	As(III), Sn(IV)	Ore	[24]
TiO <sub>2</sub> nanoparticles (salicyl fluorone in the presence of cetyltrimethylammonium bromide) <sup>a</sup>			Li(I), Cu(II), Ba(II), Cd(II), Sr(II), Co(II), Ni(II), Se(IV), Si(IV)		[27]
Coprecipitation of germanium in the presence of Mg <sup>2+</sup> , Ga <sup>3+</sup> , Ca <sup>2+</sup> and HCO <sub>3</sub> <sup>-e</sup>		0.006		Sea-, surface- and ground-waters	[17]
(Methylbenzeneazosalicylfluorone) using ultrasound-assisted leaching <sup>a</sup>	0.0– 0.72	2.75	Cr(III), Hg(II), Ti(IV), U(VI), As(III), Bi(III), Se(VI), Te(VI), Be(II), Pt(IV), Pt(II), Pd(II), Ru(IV), Ir(III), Os(VI), Au(III)	Certified reference Materials(GBW 07401 and GBW07402)	[28]
Mercapto-modified silica gel <sup>d</sup>	0.01 – 0.20	0.813	Co(II), Cu(II), Ni(II)		[8]
Kelex-100, [7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline] functional sol gel <sup>b</sup>			As(II), Sb(III), Zn(II), Ni(II)	Water	[29]
Cloud point methodology, triton X-114 <sup>d</sup>	10 – 300	0.59	As, Te, Sb	Tap and drinking water	[18]
Precipitation with Fe(OH) <sub>3</sub> and determination with trimethoxyphenylfluorone <sup>a</sup>	0 – 0.24	21	Sr(II), Pb(II), Zr(IV), Ti(IV), Mo(VI)	Foods	[23]
Chitosan functionalized with di-2-propanolamine <sup>g</sup>	0 – 0.002	50		Tap-, river-, and seawater	[30]
The separation was performed by an isocratic elution <sup>h</sup>	0.05 – 5.0			Tonic oral liquids	[31]
Anionic resin (IRA-900), catechol <sup>i</sup>				Fly ash	[32]
Modified copolymer styrene-maleic anhydride,(bis(2,3,4-trihydroxyphenylazo) benzidine in the presence of heterocyclic amines)	0.012 – 0.182	0 - 90	Cu(II), Fe(III)	Seawater and water obtained after oil pumping	[33]
ATAP Using chitosan	0.0017	0.005 – 0.075	Cu(II) and Fe(III)	seawater and water obtained after oil pumping	This work

Note: LOD: Limit of detection; Detection technique: <sup>a</sup>: spectrophotometry; <sup>b</sup>: adsorptive stripping voltammetric; <sup>c</sup>: graphite furnace atomic absorption spectrometry; <sup>d</sup>: hydride generation flame atomic absorption spectrometry; <sup>e</sup>: hydride generation-atomic emission spectrometry; <sup>f</sup>: flow injection hydride generation atomic fluorescence spectrometry; <sup>g</sup>: inductively coupled plasma mass spectrometry; <sup>h</sup>: high-performance ion-exclusion chromatography; <sup>i</sup>: atomic absorption spectrometry

than the existing procedures and that it provides a lower limit of detection. Although the procedure [32] using modified copolymer styrene-maleic anhydride, (bis(2,3,4-trihydroxyphenylazo)benzidine in the presence of heterocyclic amines) with spectrophotometry has the same selectivity, the proposed procedure has lower detection limits, in addition to lower range of determination. The proposed procedure has more advantages through the sensitivity and interference point of view. To the best of our knowledge, this is the first report of using ATAP as chromophoric reagent for preconcentration and determination of Ge(VI).

### Analytical applications

The above described preconcentration/determination of Ge(IV) was applied to samples of seawater and water obtained after oil pumping, and a comparison with the results of the reference atom-absorption analysis indicates high accuracy and precision of the proposed methodology (Table 4).

Germanium in the studied water samples exists at several ten ng L<sup>-1</sup> levels [1,11], thus, upon the treatment, it was concentrated by 175 or 200 fold. The known amounts of Ge(IV) were also spiked to water samples before pretreatment. A good agreement

**Table 4.** Determination of Ge (IV) in spiked different water samples.

Sample	Ge(IV) added ng mL <sup>-1</sup>	Proposed method		AAS method		t-test <sup>b</sup>	F-test <sup>c</sup>
		Ge(IV) Found <sup>a</sup>	Recovery %	Ge(IV) Found <sup>a</sup>	Recovery %		
Sea Water <sup>d</sup>	0	11.8	---	12	---		
	25	36.5 ± 0.81	99.18	37.6 ± 1.97	101.62	1.06	2.66
	50	61.2 ± 0.97	99.03	61.4 ± 1.42	99.03	0.82	2.11
	60	72.4 ± 0.90	100.84	71.1 ± 1.48	98.75	0.72	1.98
Sea Water <sup>e</sup>	0	12.5	---	12.4	---		
	20	32.8 ± 0.76	100.92	32.2 ± 1.84	99.38	1.87	3.76
	40	52.3 ± 0.92	99.62	52.9 ± 1.43	100.95	1.76	3.67
	60	72.1 ± 0.81	99.45	73.2 ± 1.29	101.11	1.95	3.83
Water obtained after oil pumping <sup>f</sup>	0	30.3	---	30.5	---		
	15	45.6 ± 0.87	100.66	44.9 ± 1.66	98.68	1.35	3.13
	30	60.8 ± 0.91	100.83	60.1 ± 1.48	99.34	1.66	3.59
	45	74.4 ± 1.38	98.81	76.2 ± 1.74	100.93	1.81	3.73

Note: <sup>a</sup> Mean ± Relative Standard Deviation (n=6); <sup>b</sup> Tabulated t-value for five degrees of freedom at P (0.95) is 2.57; <sup>c</sup> Tabulated F-value at P (0.95) is 5.05; <sup>d</sup> Mediterranean sea from Alexandria; <sup>e</sup> Red sea from El-Ghardaka; <sup>f</sup> Water obtained after oil pumping

between the determined and added amount of Ge(IV) has been obtained. Excellent recoveries were obtained, indicating the suitability of the sorbent for the selective collection of germanium from various water samples.

The performance of the proposed procedure was assessed by calculation of the t-value (for accuracy) and F-test (for precision) compared with the AAS method. The mean values were obtained in a Student's t- and F-tests at 95% confidence limits for five degrees of freedom [41]. The results indicated that the calculated values (Table 4) did not exceed the theoretical values. The higher accuracy, wider range of determination, increased stability and lower time consumption indicate the advantages of the proposed method over the other procedure.

## Conclusion

The results obtained demonstrate the efficiency of the chemically modified chitosan biopolymer sorbent towards selective quantitative sorption and preconcentration of Ge(IV). The sorption is markedly affected using complexing reagent, pH and surfactant, salt and time. Favorable features of the described methodology are its low instrument and running costs, simplicity, easy operation, sensitivity and high selectivity. In contrast to some other reported sorbents, the studied sorbent indicates better characteristics, as being superior in terms of selectivity, dynamic sorption capacity and detection limits, in addition to lower range of determination. The separation step results in an analytical sample which is relatively free of interferences of several ions. It can be successfully applied in routine analysis and can be applied for the determination of ultra-trace amounts Ge (IV) in a diversity of objects (environmental samples) without significant interference from other cationic species present in the samples.

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