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Preconcentration–separation of germanium at ultra trace levels on polysulfone membrane filter and its determination by spectrophotometry

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ABSTRACT

A separation–preconcentration procedure for germanium has been presented. The optimum conditions including pH, sample volume, sample-eluent flow rates, sample and matrix effects for adsorption of germanium(IV) on polysulfone membrane filter were investigated prior to spectrophotometric determination of germanium as Ge(IV)-9-phenyl-3-fluorone complex. Ge(IV) was adsorbed on membrane at pH 4.0 and was eluted from membrane with phosphoric acid. The accuracy was checked by determination of germanium content of GBW 07402 soil certified reference material. The detection and quantification limits were found as 2.1 and 7.0 ng/L, respectively. The method was applied for determination of germanium in soil and water samples.

Introduction

Germanium is a semiconductor element. It is widely used in various kinds of industry like electronic, fiber and computer, etc. [1–3]. The uses of germanium products are now increasing, and the level of germanium in the environment is beginning to rise [4]. It is an important element and has essential effects on human health [5]. The determination of trace and ultra-trace levels of germanium in environmental samples has become important [6]. Some germanium compounds have anticancer and health promotion functions so it is often used in medicines and nutriments for human [7].

Due to these points, the determination of germanium is an important part of studies in analytical chemistry. Generally a separation–preconcentration step is necessity in these studies because of low level of germanium and effects of matrix components of real samples [8–12]. Solid phase extraction, cloud point extraction, solvent extraction, microextraction and flotation have been used for the preconcentration and separation of traces of germanium in the environmental samples prior to its instrumental detection [10–16].

Membrane filtration is a preconcentration technique for traces organic and inorganic species including germanium [9,17–21]. The membrane material with a strong affinity for hydrophobic species in water are generally useful to retain the species by filtration. The collection is performed very quickly by filtration under suction with the aid of an aspirator. Adsorbed analyte species could be eluted from membrane filter with suitable eluents. In the membrane filtration technique, membrane could be used next time.

Ultra violet–visible (UV–vis) spectrophotometry is an important technique for the determination of trace analytes [22–24]. According to our literature survey, the membrane filtration of Ge(IV) on polysulfone membrane filter for preconcentration and separation of germanium in environmental samples is not used until now.

A simple and accurate membrane filtration procedure for Ge(IV) on polysulfone membrane filter has been established for separation–preconcentration of trace amounts of germanium in environmental samples prior to its spectrophotometric determination as 9-phenyl-3-fluorone complexes. The optimum conditions for adsorption of Ge(IV) ion on polysulfone membrane filter were investigated.

Experimental

Apparatus

A Hitachi 150-20 UV–vis spectrophotometer with a 1.0 cm quartz cell was used. The wavelength was set at 502.0 nm for detection of Ge(IV)-9-phenyl-3-fluorone complex. The absorbency of the complex ($\lambda max = 502$ nm) increases linearly with

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concentration up to 0.12 μg/L germanium in aqueous solution with a relative standard deviation (R.S.D.) of lower than 5%. The linear regression equation was found to be $A = 2.782C + 0.001$, where A is the absorbency, C concentration of germanium (μg/L). The linear correlation coefficient is 0.999 ($N = 5$).pH measurements were done by using Sartorius PT-10 Model pH meter with a glass-electrode. A filtering flask with a ground stopper was used for membrane filtering to the all model and real solutions.

Reagents and solutions

All chemicals used were of analytical reagent grade and were used. Distilled/deionized water (Millipore Milli-Q system 18 MΩ cm^{-1} resistivity) was used for all experiments. All glassware was kept overnight in a 10% v/v HNO_3 and then rinsed with water.

Stock germanium(IV) ion solution, 1000 mg/L, was prepared from GeO_2 (Fluka, Buchs, Switzerland) and was diluted daily for obtaining reference and working solutions. The standard solutions used for the calibration procedures were prepared before use by dilution of the stock solution with 1 M HNO_3.

9-Phenyl-3-fluorone is a member of fluorine family that is important reagents for spectrophotometric determinations of different metal ions [12–15,25–27]. 9-Phenyl-3-fluorone was purchased from Fluka (no: 78550, Buchs, Switzerland). A 0.04% (w/V) 9-phenyl-3-fluorone was prepared in ethanol and stored at 4 °C in the dark.

All membrane filters used were obtained from Osmonics (Westborough, MA). Polysulfone membrane filter (Osmonics no: 1214475) has 0.45 μm pore size and a 47 mm diameter. The buffer solutions given in literature [28,29] were used in the present work. GBW 07402 soil certificated reference material was obtained from (Beijing Century Oak Biotechnology Co., Ltd., Beijing, China).

Model procedure

Twenty five milliliter of solution containing 1.0 μg of Ge(IV) was prepared in a beaker. Two milliliter of the buffer solutions was added. After 5 min, the solution was passed through polysulfone membrane filter (0.45 μm pore size, 47 mm in diameter) by filtration under suction with an aspirator. Ge(IV) retained on the membrane filter was eluted with 5.0 mL of concentrated phosphoric acid. 0.5 mL of 10% (V/V) Triton X-100 and 1 mL of 0.04% (w/V) 9-phenyl-3-fluorone were added to this solution for complex formation between germanium(IV) and 9-phenyl-3-fluorone. Germanium content was determined by a UV–vis spectrophotometer at 502.0 nm.

Applications

A 500 mg reference material (GBW 07402 soil) or a 1.0 g soil sample was decomposed 15 mL aqua regia and the solution was evaporated to dryness. This process was repeated twice. Ten milliliter of distillated water was added to residue. Then the procedure given in the "Model procedure" section was applied. Blank samples were also analyzed.

Six hundred milliliter of water samples were placed in a beaker and adjusted to pH 4.0. Then the procedure was applied given in the "Model procedure" section for the preconcentration, separation and determination of germanium contents of them.

Results and discussion

Effect of pH

The pH of the working media is a critical parameter on the preconcentration–separation studies [30–32] for the quantitative recoveries of analyte elements. The influences of pH on the recoveries of germanium(IV) on a polysulfone membrane filter was studied in the pH range of 2.0–7.0. The results are depicted in Fig. 1. The recoveries for germanium were quantitative in the pH range of 3.5–4.5.

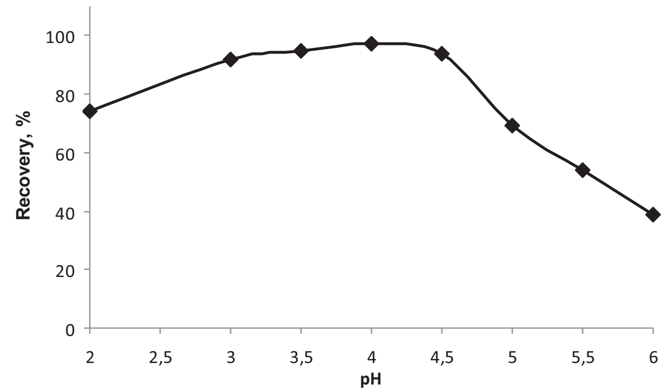

Fig. 1. The relation between pH and recovery of germanium(IV) ($N = 3$).

The influences of acetate and phosphate buffer solutions at pH 4.0 on the recovery values of germanium(IV) on polysulfone membrane filter were also investigated. The recovery values for germanium(IV) were 62 ± 0 and 98 ± 1 for acetate buffer and phosphate buffer, respectively. All further works were performed at pH 4.0 by using phosphate buffer solution.

Effects of membrane type

The effects of types of membrane filters on the germanium recoveries were also performed. The quantitative recovery values for germanium(IV) were obtained with polysulfone membrane filter (97 ± 1%). The recoveries of germanium ions were 25 ± 2% and 18 ± 0% using cellulose nitrate membrane filter and cellulose acetate membrane filter, respectively. The poor recoveries of germanium(IV) at the optimal working conditions for nitrate and cellulose acetate membranes were related poor interaction between these membranes and germanium(IV).

Reuse of filter

The effects of repeated use of polysulfone membrane filter on the recoveries of germanium(IV) was investigated under optimal working conditions. After each use, the membrane filter was cleaning with pH 4.0 buffer. The results are summarized in Table 1. Polysulfone membrane filter can be used 15 times for adsorption studies without any losses its adsorption properties. The poor recoveries after 15 usage of membrane were related with loss of membrane properties at the working conditions which was acidic media and fouling of the membrane with

Table 1
The influences of number of uses of membrane filter on the recoveries of germanium.

Number of cycle	Recovery (%)
2	97 ± 1[a]
5	96 ± 1
8	96 ± 2
10	99 ± 2
12	100 ± 2
15	96 ± 1
16	90 ± 2
18	85 ± 2

[a] Recovery% ± standard deviation.