

Choice of Inorganic Materials as $^{68}\text{Ge}/^{68}\text{Ga}$ Generator: An Intercomparison

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ABSTRACT

Adsorption properties of some inorganic oxide adsorbents were studied with varying pH conditions of HCl and HNO₃ for Ge and Ga as a trial for a ^{68}Ga generator system with their stable isotopes. Adsorption properties were also studied with varying particle size of SiO₂. Titanium oxide at its various oxidation states as well as morphological forms was also studied for similar adsorption properties. It was observed that zeolite, a microporous aluminosilicate could offer a favourable condition for use as $^{68}\text{Ge}/^{68}\text{Ga}$ generator system at pH 1 with HCl. It was also concluded that the TiO₂ powder (Degussa, P-25), which contains anatase and rutile phases in a ratio of about 3:1 can be best utilized for separation of Ga from Ge at pH 1 with HCl. This titania is a mixture of anatase and rutile particles of TiO₂ that separately form their agglomerates. Individual studies with rutile and anatase TiO₂ failed to show such effectiveness to be utilized as the above generator system.

Keywords: inorganic oxides; zeolite; Ge/Ga generator; ICP-OES

INTRODUCTION

The $^{68}\text{Ge}/^{68}\text{Ga}$ generator system is one of the most important sources for preparing radiopharmaceuticals for clinical positron emission tomography (PET), because it produces the short-lived ^{68}Ga from its long-lived parent, ^{68}Ge , over a long period [1,2]. Most popular $^{68}\text{Ge}/^{68}\text{Ga}$ generator systems are the inorganic materials such as alumina and tin dioxide which are employed as adsorbents for ^{68}Ge .

In the $^{68}\text{Ge}/^{68}\text{Ga}$ generator system consisting of an alumina column, ^{68}Ga is eluted with ethylenediaminetetraacetic acid (EDTA) solution as a ^{68}Ga -EDTA complex. If it could be available for radiopharmaceutical labeling, this method would be desirable; however, it requires some additional complicated operations for the

preparation of other radiopharmaceuticals because of the high stability of the complex [3]. The ^{68}Ga build up on a tin dioxide column can be eluted in ionic form with 1 M HCl.

However, this method also needs a neutralization step. In addition, contaminant metals (i.e., aluminum and tin) are present in significant amounts in the eluate [4]. A $^{68}\text{Ge}/^{68}\text{Ga}$ generator system based on CeO₂ as adsorbent was also developed. In this case sharp elution curves were obtained using 0.02 M HCl and no radioactive impurities or dissolved cerium were found in the eluate [5]. Atomic absorption studies indicated absence of elemental impurities in the eluate.

Studies on the influence of preliminary annealing at 1000 °C and wet treatment with HCl and NaOH on aluminium oxide were done on the separation efficiency of ^{68}Ge - ^{68}Ga radionuclides. A desorption degree of 55% for ^{68}Ga was observed after pretreatment procedures [6].

$^{68}\text{Ge}/^{68}\text{Ga}$ generator system with an organic polymer having a high affinity for germanium and a low affinity for gallium, has also been studied so far [7]. The organic polymer containing 1-deoxy-1-(methylamino) sorbitol (*N*-methylglucamine) group effectively adsorbs ^{68}Ge in buffer solution above pH 5. The ^{68}Ga built by the decay of ^{68}Ge was separated from the resin with a solution of a low-affinity gallium chelating ligand such as citric or phosphoric acid. But the problem with organic polymers is that they have low radiation stability compared to the inorganic materials.

In the present paper we report the relative abilities of different inorganic materials as probable adsorbers for an efficient $^{68}\text{Ge}/^{68}\text{Ga}$ generator system at different pH at mM concentrations of stable Ge and Ga using batch extraction method.

EXPERIMENTAL

TiO_2 (Degussa AG P25), ZnO (MERCK, Germany), SnO_2 (Fluka, Amsterdam), Zeolite (Zeolyst International), Al_2O_3 (Fluka 100-125 mesh) and SiO_2 (MERCK Germany 0.08 mm) were studied for their Ge and Ga uptake using the batch extraction method at varied pH conditions using two monoprotic mineral acids HCl and HNO_3 . 100 mg of each of the oxide adsorbers were preconditioned with different acid concentrations. 100 μL solutions containing equal concentrations of Ge and Ga in the form of standard solutions in HNO_3 were added to the pretreated oxide adsorbers in such way that the final concentrations of Ge and Ga were each of 0.1 ppm. The systems were shaken for 10 minutes and then centrifuged to collect the clear upper solution for measurement in the ICPOES for Ge and Ga (Perkin Elmer, Optima 4300).

The results were compared with standards prepared in the same way but without the adsorber material. The weights of the

adsorbers were also varied with higher weights for adsorption of same amounts of the elements to confirm the maximum material required. Two of the materials, silica and titania were also varied for their mesh size and solid form respectively to observe any variation in uptake properties. SiO_2 , (14-20 mesh, Aldrich Chemie), SiO_2 (0.08 mm, MERCK), SiO_2 (1-3 mm, Fluka, Amsterdam) SiO_2 (60-120 mesh BDH chemicals, England), SiO_2 (0.2-0.5 mm, Fluka, Amsterdam) were the silica samples of different particle sizes used to study the uptake properties of Ge and Ga. Titanium (II) oxide (-325 mesh, Aldrich), titanium (III) oxide (-100 mesh, Aldrich), TiO_2 (rutile, <5 microns, Aldrich) and TiO_2 (anatase, -325 mesh, Aldrich) were also studied for similar uptake properties.

RESULTS AND DISCUSSION

The TiO_2 (Degussa AG P25) has a specific surface area of 57.4 m^2/g , and the phase composition of 70% anatase and 30% rutile. This kind of titania is a mixture of anatase and rutile particles of TiO_2 that separately form their agglomerates. The average sizes of the anatase and rutile elementary particles being 85 and 25 nm, respectively [8]. The zinc oxide is a stable compound with a wurtzite-type hexagonal structure and has a specific surface area of 3.95 m^2/g [9]. The SnO_2 has a very high specific surface area of 141.6 m^2/g and the crystal structure conforms to cassiterite-tetragonal [10]. Powder samples of NaY zeolite (CBV100) supplied by Zeolyst International has a surface area of 900 m^2/g and has $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 5.1 [11]. The $\gamma\text{-Al}_2\text{O}_3$ (100-125 mesh) has a surface area of 173 m^2/g and the detailed crystal structure is available in the literature [12,13]. The SiO_2 has a surface area of 750 m^2/g and a tetrahedral structure [14].

Figures 1-6 give an idea about the adsorption properties of Ge and Ga on the oxide adsorbers at different pH conditions. It could be observed that except for TiO_2 and SnO_2 all the others have better affinity for Ga rather than Ge at higher pH conditions.

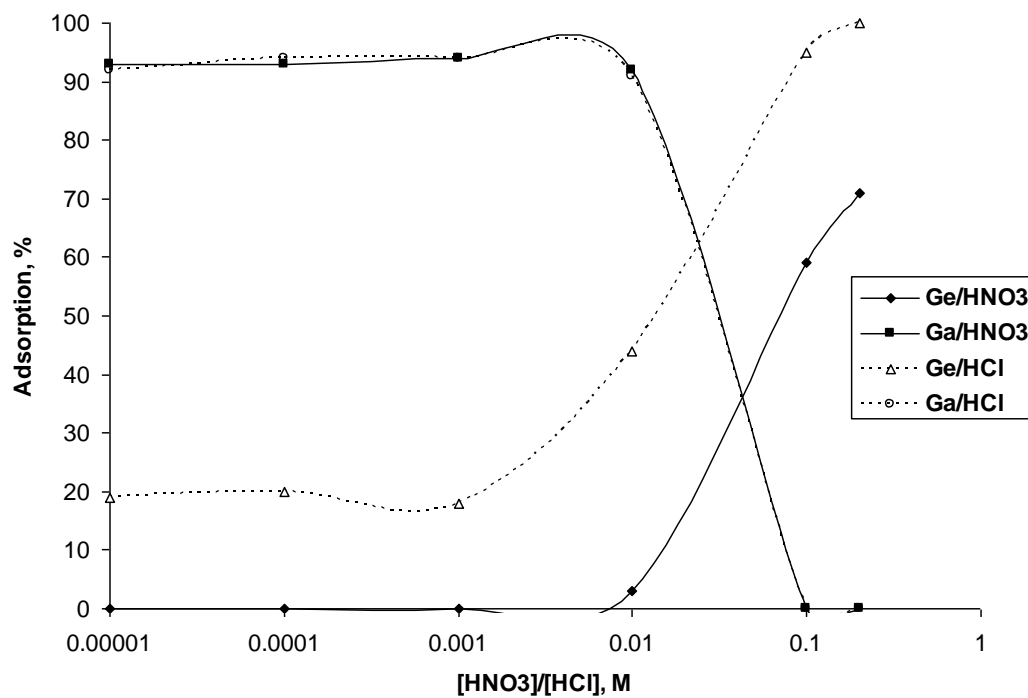


Figure 1: Adsorption profile of Ge and Ga in Zeolite with varying pH of HCl and HNO_3 .

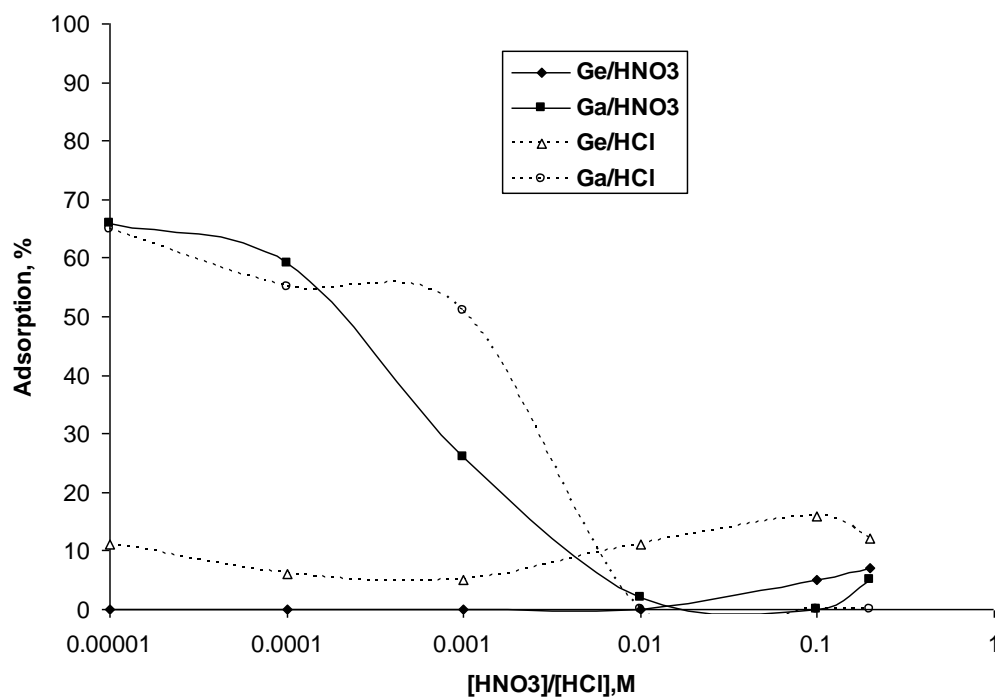


Figure 2: Adsorption profile of Ge and Ga in SiO_2 with varying pH of HCl and HNO_3 .

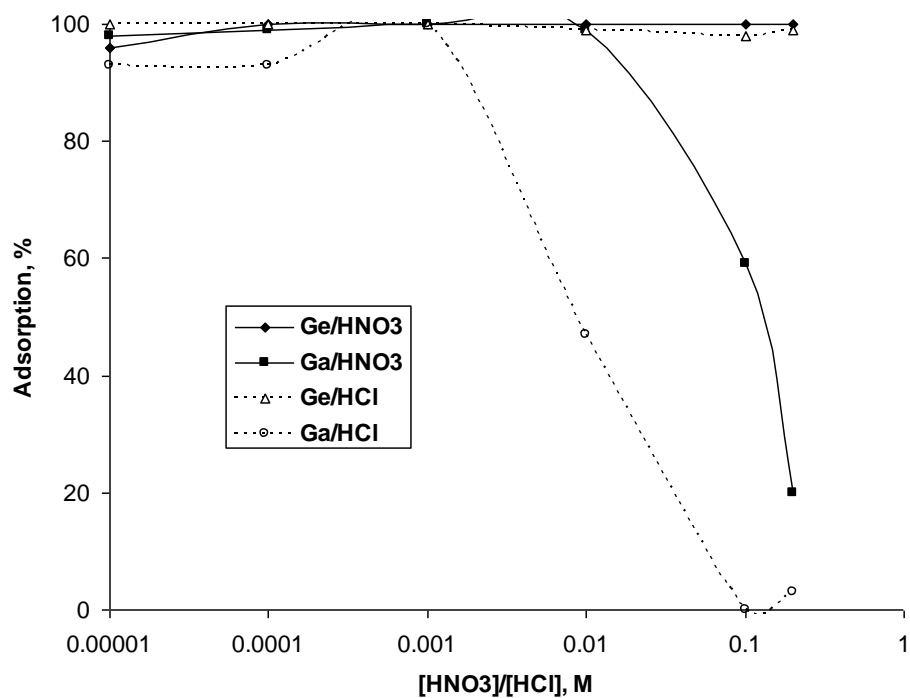


Figure 3: Adsorption profile of Ge and Ga in TiO₂ with varying pH of HCl and HNO₃

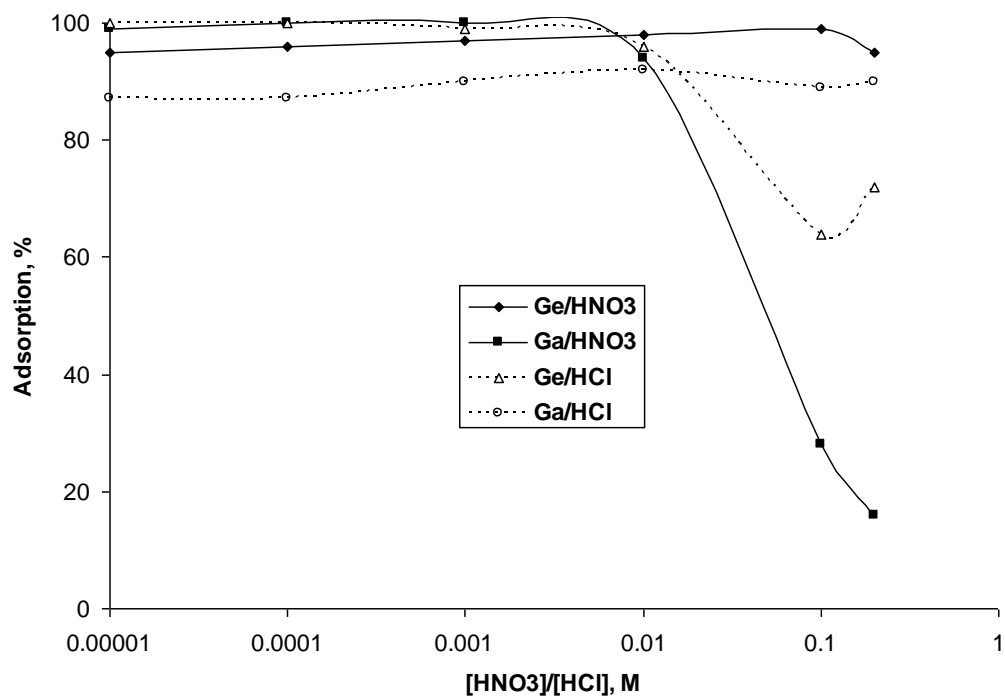


Figure 4: Adsorption profile of Ge and Ga in ZnO with varying pH of HCl and HNO₃

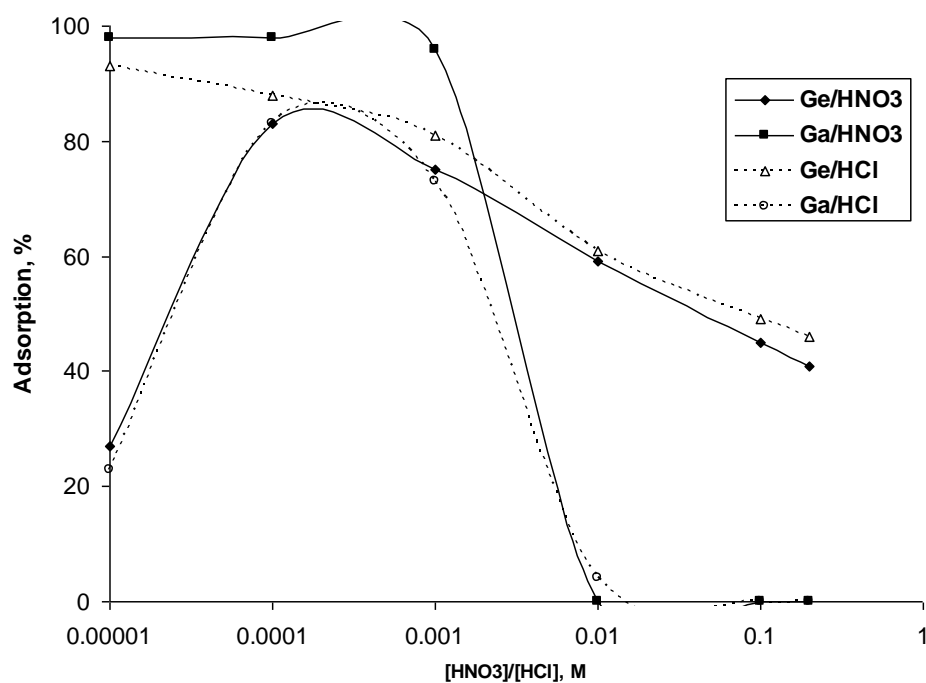


Figure 5: Adsorption profile of Ge and Ga in Al_2O_3 with varying pH of HCl and HNO_3

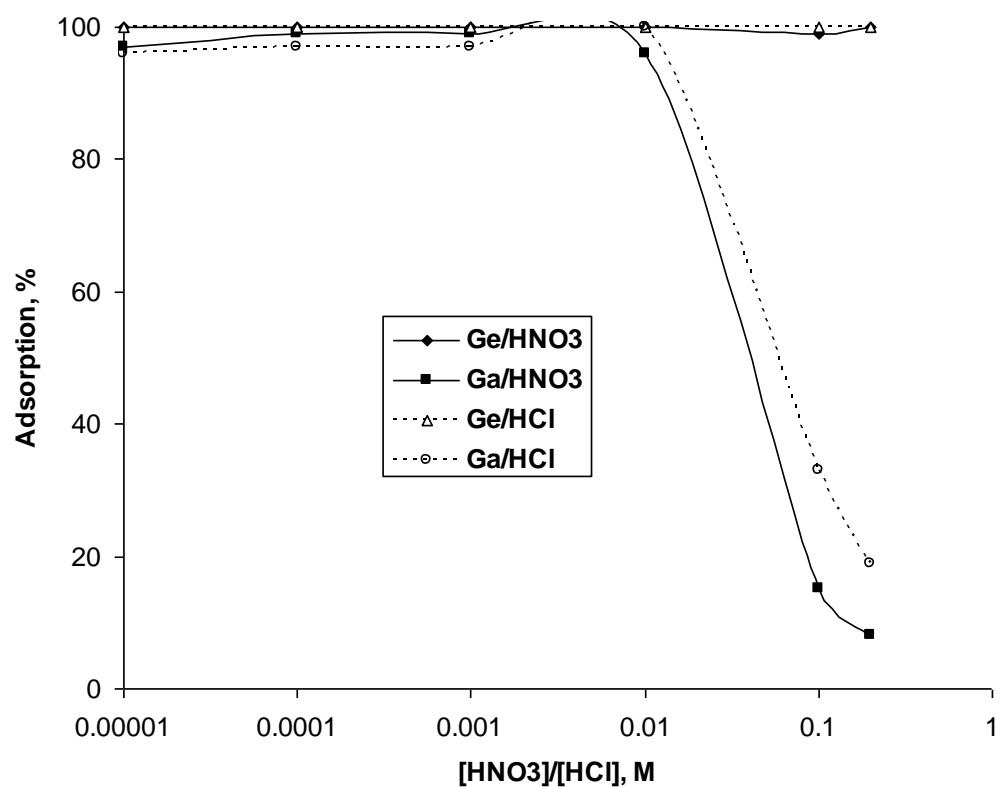


Figure 6: Adsorption profile of Ge and Ga in SnO_2 with varying pH of HCl and HNO_3

There was an interesting observation with zeolite (figure 1). There was a cross over of adsorption affinity for Ge and Ga around pH 1. At higher pH the exchanger was selective for Ga rather than Ge. However at and below pH 1 acidity of HCl, zeolite adsorbs Ge and has no affinity for Ga. This information can be used as a tool both to find zeolite as a generator as well as in the purification step in Ge/Ga generator systems [15].

The isoelectric points (IEP) of metal oxides are used extensively in material science in various aqueous processing steps [16]. For these surfaces, present as colloids or larger particles in aqueous solution, the surface is generally assumed to be covered with surface hydroxyl species, $M-OH$ (where M is a metal such as Al, Si, etc.). At pH values above the IEP, the predominate surface species is $M-O^-$, while at pH values below the IEP, $M-OH_2^+$ species predominate. The uptake of Ge and Ga on these oxides was not found to be exactly dependent on their respective IEP (table 1).

Table 1: Isoelectric points of the inorganic oxides used as adsorber for Ge/Ga system

Oxide	Isoelectric Point (IEP)
TiO ₂	4
ZnO	9
SnO ₂	6
Zeolite	-
Al ₂ O ₃	9
SiO ₂	2

The theoretical programme on the species calculations, "CHEAQS" indicate that Ga remains as Ga^{+3} species in solution at or below pH~3 [17]. Above this pH Ga remains as mixed hydroxide species. As the IEP values of most of the oxides are above pH 3 (except silica, at pH 2) the sudden drop in adsorption of Ga below pH 3 could attributed to the repulsion between same charges on the adsorber and Ga.

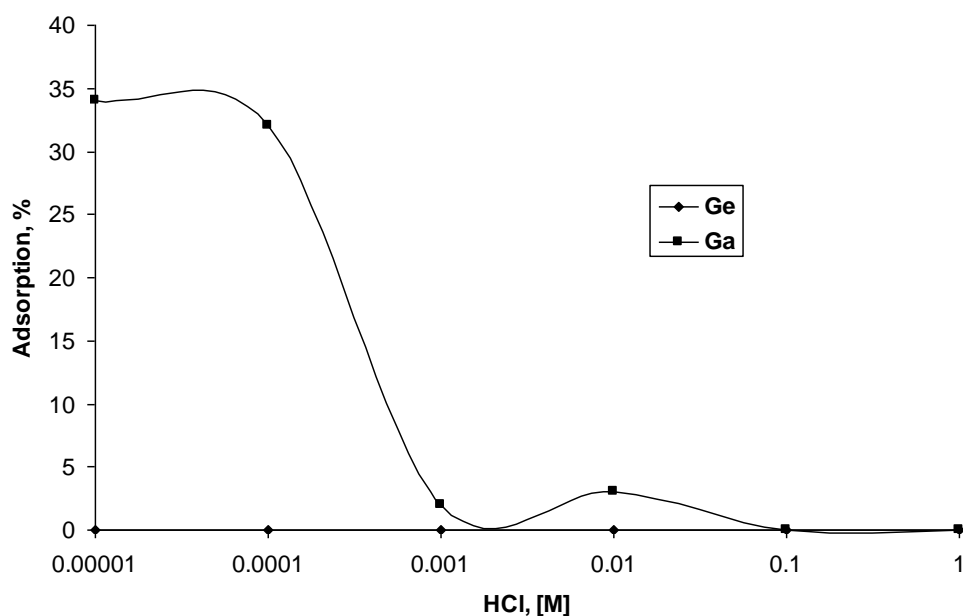


Figure 7: Adsorption profile of Ge and Ga in SiO₂ (14-20 mesh) with varying pH of HCl

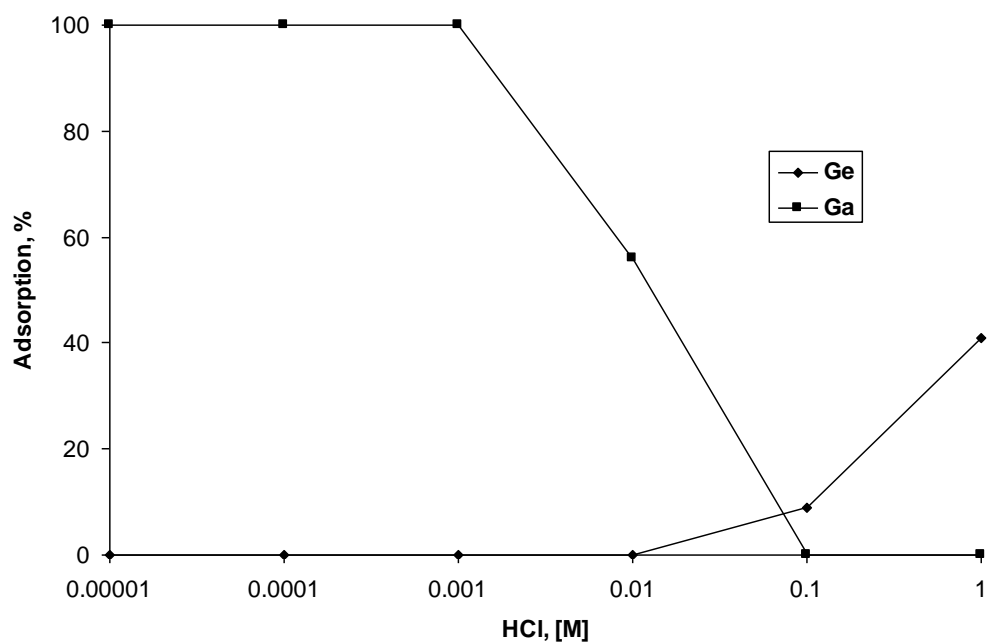


Figure 8: Adsorption profile of Ge and Ga in SiO₂ (0.08 mm) with varying pH of HCl

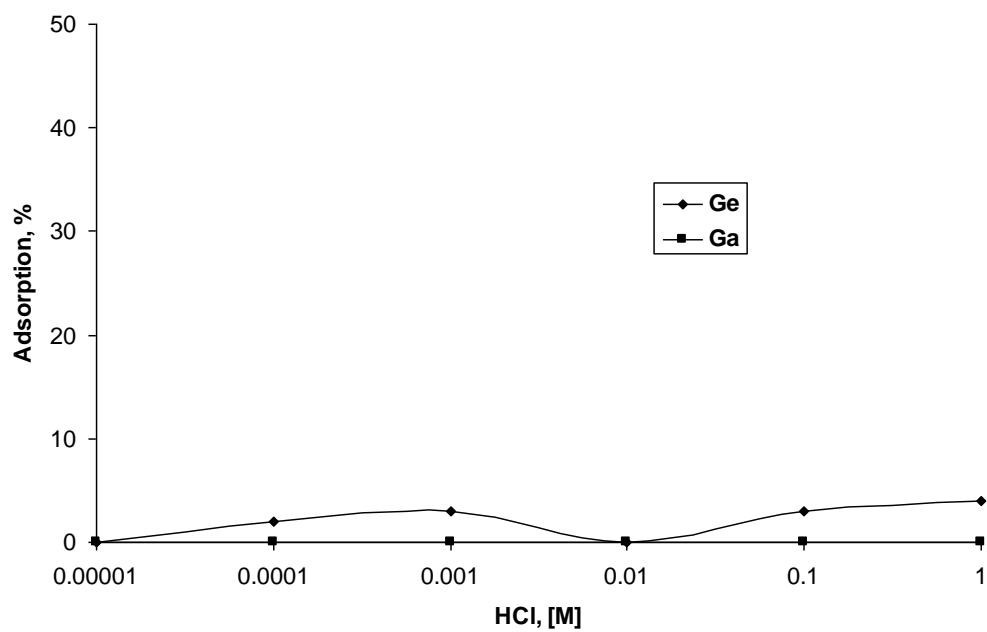


Figure 9: Adsorption profile of Ge and Ga in SiO₂ (1-3 mm) with varying pH of HCl

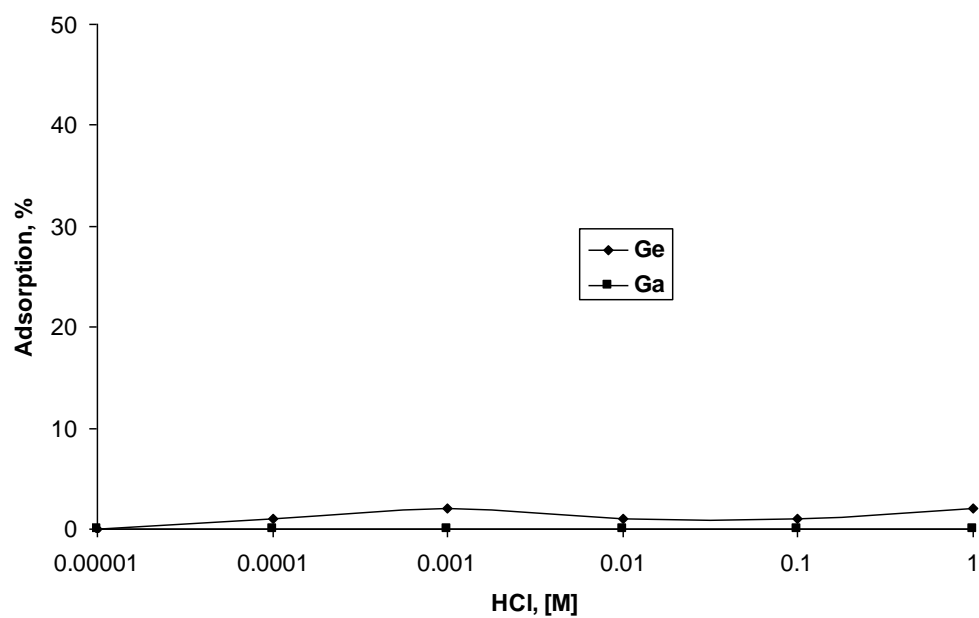


Figure 10: Adsorption profile of Ge and Ga in SiO₂ (60-120 mesh) with varying pH of HCl

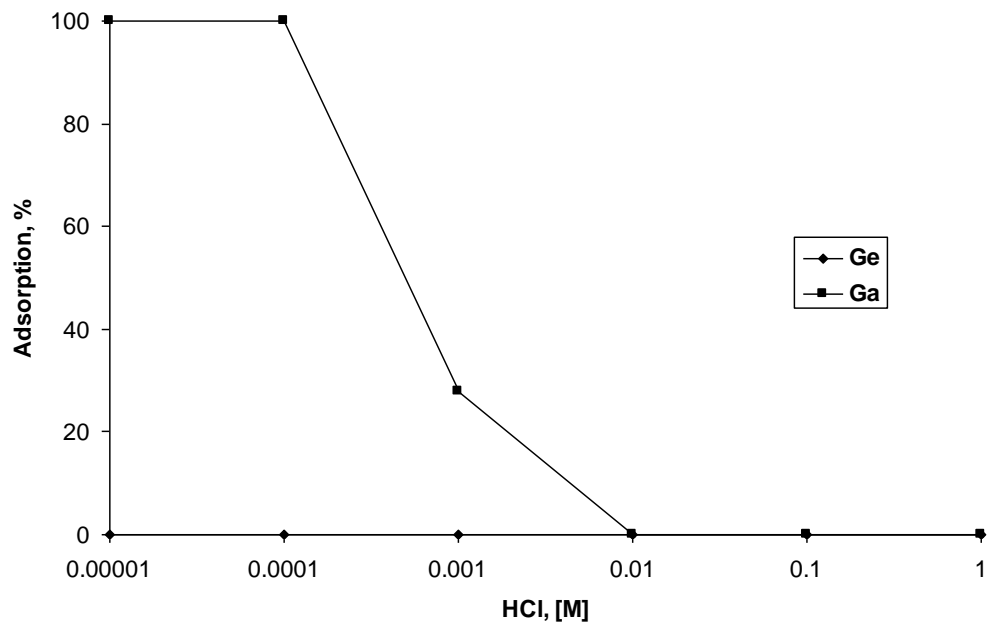


Figure 11: Adsorption profile of Ge and Ga in SiO₂ (0.2-0.5 mm) with varying pH of HCl

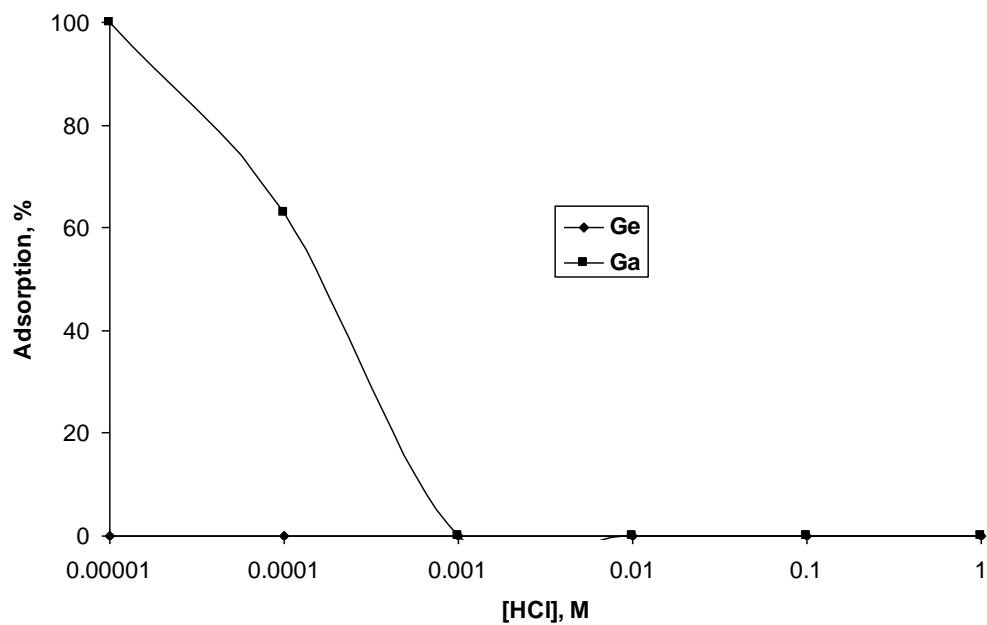


Figure 12: Adsorption profile of Ge and Ga in TiO with varying pH of HCl

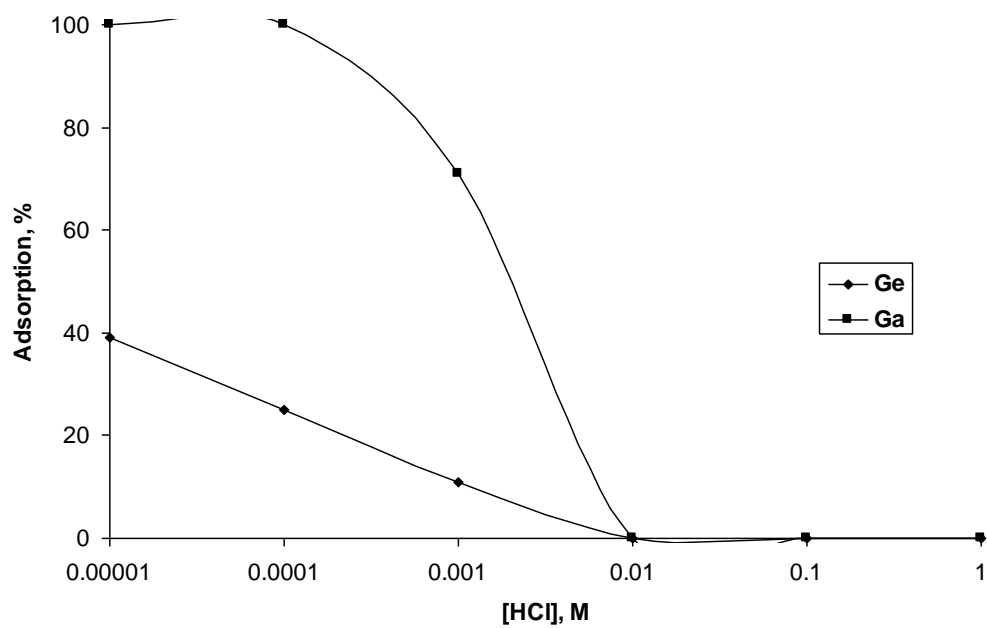


Figure 13: Adsorption profile of Ge and Ga in Ti₂O₃ with varying pH of HCl

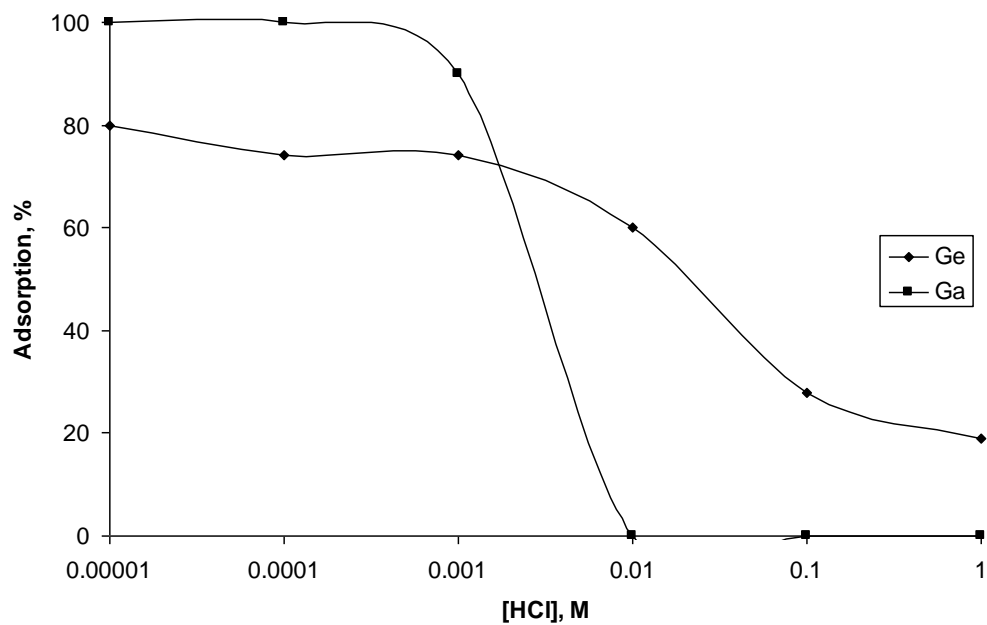


Figure 14: Adsorption profile of Ge and Ga in TiO₂ (Rutile) with varying pH of HCl

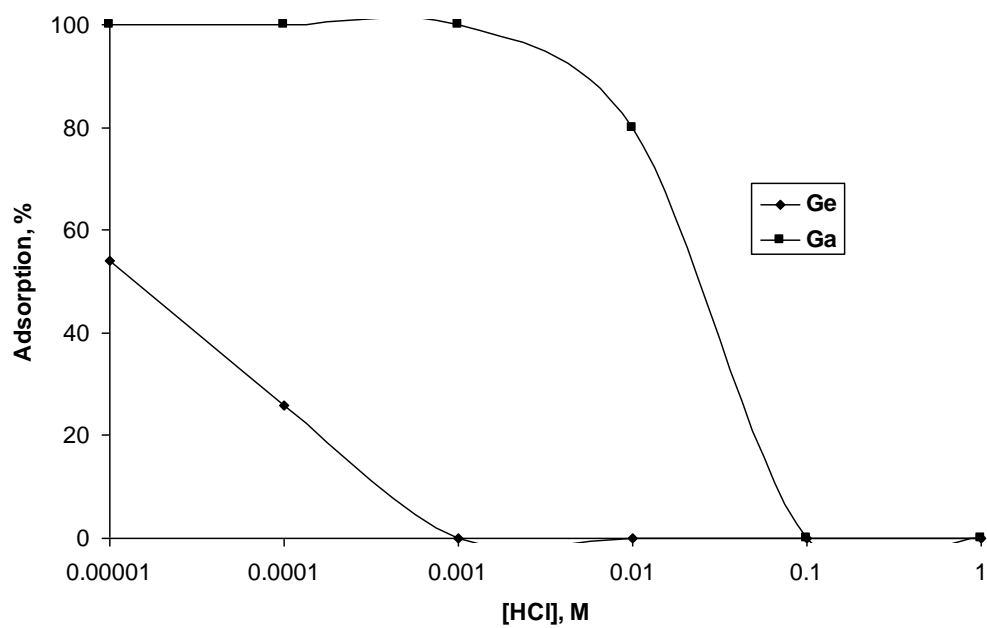


Figure 15: Adsorption profile of Ge and Ga in TiO₂ (Anatase) with varying pH of HCl

Amongst all the particle sizes studied (Figure 7-11) the silica particle of sizes 0.08 mm and 0.2-0.5 mm show a clean separation over the pH range 4-5 between Ga and Ge (Figure 8 and 11). The adsorption on SiO₂ surface is probably not caused due to insertion inside the tetrahedron. Rather the isoelectric pH of the oxide material (~2 for SiO₂ as presented in table 1) is responsible for charge interactions in the adsorption process. It could be deduced that the above two sized particles may be used in the purification step for Ga. The fact that the required acidity for this step with silica is very low also seems to be an advantage for further labelling studies with ⁶⁸Ga radioisotope.

The Ti(II) as well as Ti(III) oxides were not found to be very effective for any adsorption and separation for Ge and Ga at the pH range studied (Figures 12 and 13). The TiO₂ powder (Degussa, P-25), which is a standard material in the field of photocatalytic reactions, contains anatase and rutile phases in a ratio of about 3:1 [18]. Transmission electron microscopy was used by Ohno et al., to prove that the anatase and rutile particles separately form their agglomerates. They found that the average sizes of the anatase and rutile elementary particles are 85 and 25 nm, respectively. Figures 14 and 15 indicate that there is a higher affinity of Ga for both the rutile and anatase phases of TiO₂ separately at the pH range 3-5. In addition there is no possibility of separation between Ge and Ga. However in the P25 solid where the anatase and rutile agglomerate particles are in contact, leads to a synergy effect and the adsorption properties are vastly different as could be seen from figure 3.

CONCLUSIONS

The article gives a concise idea about the comparative ability of different inorganic oxides to be used a generator for ⁶⁸Ge/⁶⁸Ga. It was observed that zeolite, a microporous aluminosilicate could offer a favourable condition for use as Ge/Ga generator system at pH 1 with HCl. There was a cross over of adsorption affinity for Ge and Ga around pH 1. At higher pH (above 1) the exchanger was selective for Ga rather than Ge.

However, at and below pH 1 acidity of HCl, zeolite adsorbs Ge and has no affinity for Ga. This information can be used as a tool both to find zeolite as a generator as well as in the purification step in Ge/Ga generator systems. Similar studies with varying particle size of

titania revealed that the TiO₂ powder (Degussa, P-25), which contains anatase and rutile phases in a ratio of about 3:1 can be best utilised for separation of Ga from Ge at pH 1 with HCl. Individual studies with rutile and anatase TiO₂ failed to show such effectiveness to be utilized as the above generator system.

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