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Johann Korkisch[a]; Franz Feik[a]
[a] ANALYTICAL INSTITUTE, UNIVERSITY OF VIENNA, VIENNA, AUSTRIA

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Anion-Exchange Separation of Germanium from Arsenic(III and V) and Other Elements in Hydrochloric Acid–Acetic Acid Medium

JOHANN KORKISCH and FRANZ FEIK
ANALYTICAL INSTITUTE,
UNIVERSITY OF VIENNA,
VIENNA, AUSTRIA

Summary

In this paper a highly selective method is described for the separation of micro- and milligram amounts of germanium from arsenic(III and V) as well as from many other metal ions by means of the strongly basic anion-exchange resin Dowex 1-X8. This separation procedure is based on the preferential elution of germanium tetrachloride from a column of this resin by means of a mixture consisting of 90% acetic acid and 10% 9 *N* hydrochloric acid, under which condition arsenic, iron, cobalt, copper, manganese, molybdenum, lead, bismuth, and several other metal ions are strongly retained by the resin as anionic chlorocomplexes while germanium passes into the eluate practically unadsorbed. For the final photometric determination of germanium directly in the eluate, a modification of the phenylfluorone method is employed.

The methods most frequently used for the analytical separation of microgram and milligram quantities of germanium from other elements are based either on the extraction or distillation of germanium tetrachloride. In the first case germanium from strong hydrochloric acid solution is extracted into carbon tetrachloride; in the second case the volatile chloride is distilled from solutions of comparable acidity with respect to hydrochloric acid concentration. Both methods are of about equal effectiveness in separating germanium from elements interfering with its final quantitative determination, which is, in most cases, carried out by using the phenylfluorone method, especially when microgram amounts of germanium are involved.

Of much less importance so far have been chromatographic procedures and methods based on coprecipitation, because of their relatively low selectivity.

Besides cation-exchange methods, several papers have appeared in the literature dealing with the separation of germanium from other elements by means of anion exchange. Germanium as the anionic chloride complex is strongly adsorbed, e.g., on Dowex 1 from pure aqueous solutions at hydrochloric acid concentrations ranging from about 8 to 10 *N* hydrochloric acid with distribution coefficients increasing from 80 to about 400, respectively (5,9). Based on this fact, germanium can be readily separated from metal ions, forming weaker or no anionic complexes under these conditions—complexes such as arsenic(V), the rare earth elements (*5,10*), thorium, nickel, aluminum, etc. However, no separation is possible from arsenic(III), iron(III), cobalt(II), uranium(VI), manganese(II), and several other metal ions that form rather strong anionic chlorocomplexes under these conditions. Because germanium is not appreciably retained at lower hydrochloric acid concentrations, e.g., from 3 *N* hydrochloric acid, its separation from some of these stronger adsorbed elements, as, for instance, from iron(III), uranium(VI), etc., is also possible, but not from arsenic (III), cobalt(II), manganese(II), and other elements (*6*). Recently a method for the separation of germanium from arsenic(III) was described (*1*) which is based on the adsorption of germanium on a column of the anionite ÉDÉ-10P (chloride form) while arsenic passes through. The germanium is subsequently eluted with 9 *N* hydrochloric acid.

A sequential separation of indium, lead, germanium, tin, and bismuth can be effected by using as eluants 0.1 *N* HCl–1 *N* HF (for indium and lead), 6 *N* HCl–1 *N* HF (for germanium), 2 *N* HCl–3 *N* HF [for tin(IV)], and 1 *M* ammonium chloride–1 *M* ammonium fluoride (for bismuth) (*7*).

Similar to its behavior toward Dowex 1, germaniun is appreciably extracted with the secondary amine Amberlite LA-1 (N-dodecenyltrialkylmethylamine) dissolved in xylene when the extraction is performed from solutions with a hydrochloric acid concentration exceeding 7 *N* (*4*). Back-extraction of germanium may be effected with 0.5 to 1 *N* hydrochloric acid.

The adsorption of germanates on Amberlite IRA-400 over the pH range 6 to 12 in the presence of ethylene glycol, glycerol, and mannitol was also studied (2), but no analytical application of these investigations have been reported.

From this literature survey it is seen that none of the methods so far developed for the anion-exchange separation of germanium is suitable to separate this element from a very large group of elements.

Because earlier investigations have shown (3) that in mixed aqueous-organic solvent systems many separations of metal ions in the presence of hydrochloric or other mineral acids can be effected with a much higher selectivity, such media have been investigated here to effect a separation of germanium from many other metal ions, including arsenic(III).

EXPERIMENTAL

Reagents and Solutions

The strongly basic anion-exchange resin Dowex 1-X8 (100–200 mesh, chloride form) was used. Further used were standard solutions of germanium tetrachloride and of the chlorides of many other elements in 9 *N* hydrochloric acid. The reagent-grade organic solvents employed were glacial acetic acid, methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol, methyl glycol (2-methoxy-ethanol-1), ethyl glycol (2-ethoxy-ethanol-1), tetrahydrofuran, acetone, and propionic acid.

The acetic acid–hydrochloric acid mixture was prepared by mixing 9 parts of glacial acetic acid with 1 part of 9 *N* hydrochloric acid. When disregarding the slight volume changes due to mixing, this solution is 90 vol. % in acetic acid and 10 vol. % in 9 *N* hydrochloric acid.

Apparatus

The separation experiments were performed on 1- and 10-g resin columns with diameters of 0.5 and 1 cm, respectively. For determination of the distribution coefficients of germanium and arsenic(III and V), 1-g resin columns were used.

Procedure: Separation of Germanium from Arsenic(III and V) and Other Metal Ions

Through the resin bed (10-g column) pretreated with 50 ml of the acetic acid–hydrochloric acid mixture, 10 ml of the sample solution 90% in acetic acid and 10% in 9 *N* hydrochloric acid, containing germanium, arsenic, or other elements to be separated from it, is passed at a flow rate of 1 ml/4.5 min. Under these conditions arsenic(III and V), and most of the other elements, are retained on top of the resin bed while germanium passes into the eluate. For the complete elution of amounts of germanium around 14 mg, the column has then to be washed with 35 ml of the acetic acid–hydrochloric acid mixture. If washing with this mixture is continued beyond another 5 to 7 ml, arsenic(III), as well as other metal ions which are only slightly retained by the resin, start to break through.

For the photometric determination of germanium in the eluate by means of phenylfluorone, procedure A, as described by Sandell (*8*, p. 489) was modified to be directly applicable to the germanium-containing eluate obtained after carrying out the column operation described above. If necessary the eluate is diluted with the acetic acid–hydrochloric acid mixture to give a final solution of which 3 ml contains germanium in amounts ranging from 10 to 25 μg. Such a 3-ml aliquot is transferred to a 50-ml measuring flask and the following reagents are added: 5 ml of gum arabic solution [see Sandell (*8*, p. 489)]. 4 ml of concentrated hydrochloric acid, 18 ml of water, and 15 ml of phenylfluorone solution [see Sandell (*8*, p. 489)]. After dilution to 50 ml with water, the absorbance of the solution is measured after 30 min at 510 mμ using a reagent blank solution as reference. Under these conditions the absorbance is 0.100 if 10 μg of germanium is present in 50 ml of measuring solution. Beer's law is strictly obeyed from 0 to 30 μg germanium/50 ml.

The distribution coefficients of germanium and of arsenic(III and V) as well as the adsorption characteristics of many other elements were determined using the column method; i.e., the elution curves were recorded on 1-g columns of the resin. Under these conditions the retention volume (volume corresponding to the elution peak of the element in question) in milliliters is roughly equal to the distribution coefficient of the element. At the same time the breakthrough and elution volumes were determined. For these studies 0.14 and 1.0 mg amounts of germanium and the other elements dissolved in 2 ml of hydrochloric acid–organic solvent mixtures were used. The flow rate corresponded to 1 ml/4.5 min. The breakthrough, retention, and elution volumes were detected by using sensitive color reactions for the elements concerned.

RESULTS

From Table 1, showing the elution characteristics of germanium and arsenic(III and V) when using 90% organic solvent–10% 6 *N* hydrochloric acid mixtures as eluants, it is seen that for a quantitative chromatographic separation of germanium from arsenic(III) the most suitable medium is that which contains acetic acid as the organic component. Under these conditions the germanium is just completely eluted when the arsenic starts to break through. All the other investigated systems are unsuitable, because a serious overlapping of elution curves occurs; that is, the elution volumes

TABLE 1

Elution Characteristics of Germanium and Arsenic(III and V) on 1-g Columns of Dowex 1-X8 Using as Eluants 90 Vol. % Organic Solvent–10 Vol. % 6 *N* Hydrochloric Acid Mixtures

	Ge(IV)			As(III)			As(V)		
Organic solvent	BTV,[a] ml	VEP,[b] ml	EV,[c] ml	BTV, ml	VEP, ml	EV, ml	BTV, ml	VEP, ml	EV, ml
Methanol	4	6	9	2	4.5	7	2	3.5	7
Ethanol	6	10.5	17	3	5	7	4	6.5	11
n-Propanol	2	3.5	14	2	3	6	2	5	10
Isopropanol	9	11.5	19	4	6	10	5	7.5	12
n-Butanol	12	15.5	20	3	5	9	5	9.5	14
Isobutanol	11	13	18	3	5.5	10	6	10	14
Methyl glycol	3	4.5	8	3	4	7	4	6	8
Ethyl glycol	3	4.5	9	2	4	7	4	6	12
Tetrahydrofuran	6	10.5	17	3	5	7	4	6.5	11
Acetone	2	3.5	7	2	4	8	2	6.5	9
Acetic acid	2	4	6	6	9	13	8	10	16
Propionic acid	3	4.5	7	5	7.5	10	12	16.5	22
Water	2	3.5	6	2	4	7	2	4	7

[a] BTV, breakthrough volume.
[b] VEP, volume of elution peak (retention volume) ≅ distribution coefficient (K_d).
[c] EV, elution volume.

of germanium in these media are always greater than the breakthrough volumes of arsenic(III). However, separation of germanium from arsenic(V) can be achieved not only in an acetic acid but also in a propionic acid medium, but in the latter incomplete separation of germanium from arsenic(III) results.

The detailed study of the elution behavior of these two valency states of arsenic represented in Table 1 was carried out because arsenic is the element which is the most difficult to separate from germanium, and usually accompanies germanium when it is separated from other elements by conventional methods such as extraction or distillation of germanium tetrachloride.

To improve the separability of germanium in the acetic acid–hydrochloric acid mixtures, several experiments were performed in acetic acid–hydrochloric acid systems by replacing part of the acetic acid by carbontetrachloride or chloroform (the solvents most frequently used in the liquid-liquid extraction of germanium tetrachloride) and by increasing the concentration of hydrochloric acid in the 90% acetic acid–10% hydrochloric acid medium. From the results as represented in Table 2 it is seen that the most suitable elution characteristics are obtained in a 90% acetic acid–10% 9 *N* hydrochloric acid medium. For this reason this medium was

TABLE 2

Elution Characteristics of Germanium and Arsenic(III and V) on 1-g Columns of Dowex 1-X8 Using as Eluants Acetic Acid–Hydrochloric Acid Mixtures

	Ge(IV)			As(III)			As(V)		
Composition of eluant	BTV, ml	VEP, ml	EV, ml	BTV, ml	VEP, ml	EV, ml	BTV, ml	VEP, ml	EV, ml
90 vol. % AA[a]–10 vol. % 6 *N* HCl	2	4	6	6	9	13	8	10	16
90 vol. % AA–10 vol. % 9 *N* HCl	2	3.5	5	6	9.5	13	7	11.5	17
80 vol. % AA–10 vol. % CCl_4–10 vol. % 6 *N* HCl	2	3.5	7	5	6.5	10	5	7.5	12
80 vol. % AA–10 vol. % $CHCl_3$–10 vol. % 6 *N* HCl	3	4	7	5	7.5	12	9	12	23

[a] AA = acetic acid.

TABLE 3

Separation of Varying Amounts of Germanium and Arsenic(III) on 10-g Columns of Dowex 1-X8 Using as Eluant a 90 Vol. % Acetic Acid–10 Vol. % 9 *N* Hydrochloric Acid Mixture

Used amount of germanium, μg	Amount of arsenic(III) simultaneously present, mg	Recovered amount of germanium, μg	Error, %
14	1.6	14.2	1.4
14	2.4	14.1	0.7
14	3.2	13.9	−0.7
140	1.6	142	1.4
140	2.4	140	±0.0
140	3.2	143	2.1
1400	1.6	1408	0.56
1400	2.4	1397	−0.49
1400	3.2	1395	−0.35

selected for all further investigations as well as for the separation of varying amounts of germanium and arsenic(III) when present in micro- and milligram quantities.

By employing the working procedure described above, the results listed in Table 3 were obtained. They show that good separa-

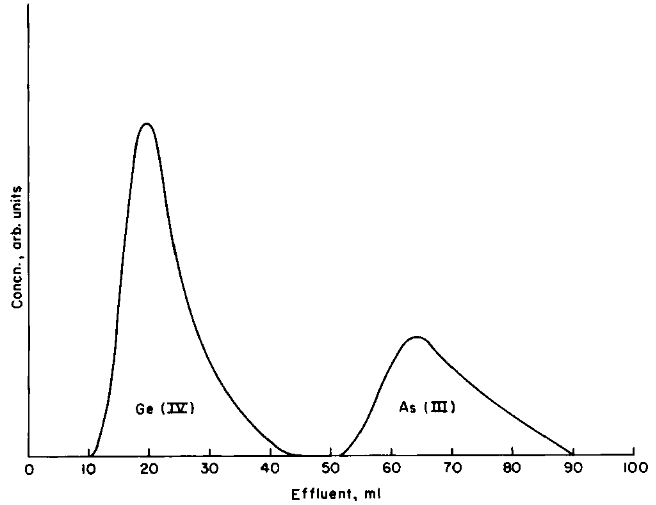

FIG. 1. Separation of 14 mg of germanium from 3.2 mg of arsenic(III) on a 10-g column of Dowex 1-X8 using 90 vol. % acetic acid–10 vol. % 9 *N* hydrochloric acid mixture and a flow rate of 1 ml/4.5 min.

tion of these elements can be achieved in a concentration range of germanium which varies by two orders of magnitude.

To demonstrate more clearly the effectiveness with which these separations can be carried out, typical elution curves obtainable under these experimental conditions are shown in Fig. 1. Investigations concerning the adsorption behavior of 22 other metal ions from a 90% acetic acid–10% 9 *N* hydrochloric acid mixture gave the results shown in Table 4. From these results it is seen that only calcium, magnesium, nickel, and some chromium will accompany germanium into the eluate; i.e., the breakthrough volumes of these metal ions are smaller or equal to the elution volume of germanium. Of these elements only chromium interferes with the spectrophotometric determination of germanium when using the phenylfluorone

TABLE 4

Elution Characteristics of Metal Ions on 1-g Columns of Dowex 1-X8 (1 mg load) Using as Eluant 90 Vol. % Acetic Acid–10 Vol. % 9 *N* Hydrochloric Acid

Metal ion	BTV, ml	VEP, ml	EV, ml
Ge(IV)	2	3.5	5
Ca(II)	2	4	8
Mg(II)	3	7	12
Ni(II)	3	5	10
Cr(III)	5	12	45
V(IV/V)	10	15	50
Ce(III)	7	13	42
Th(IV)	20	>50	>100
Fe(III)	↑	↑	↑
Co(II)			
Cu(II)			
Mn(II)			
Au(III)			
Zn(II)			
Cd(II)	≥30	Not determined	Not determined
Hg(II)			
In(III)			
Sn(II and IV)			
Pb(II)			
Sb(III)			
Bi(III)			
Mo(VI)			
UO_2(II)	↓	↓	↓

method. By the use of a suitably long column even this element can be quantitatively separated from germanium, because the separation factor [K_d chromium(III)/K_d germanium(IV)] is about 3.4.

All the other elements listed on Table 4 can readily be separated from germanium because they are retained by the resin as anionic chloride complexes. These include thorium, which from pure aqueous hydrochloric acid solutions is not retained by the resin even from concentrated hydrochloric acid.

Conclusively it should be pointed out that this separation method of germanium from arsenic and the other elements can, because of its rather high selectivity, be employed to solve many problems encountered in the analytical chemistry of germanium, and if performed on a macro scale it might be of importance concerning the purification of germanium used as semiconductors or for other purposes.

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