Column chromatographic separation of gallium(III) from other elements using poly(dibenzo-18-crown-6)

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Poly(dibenzo-18-crown-6) has been used for the separation of gallium(III) from indium(III), thallium(III) and other elements in hydrochloric acid medium. The capacity of poly(DB-18-C-6) for gallium is found to be 0.932 mmol/g. The separation has been described in binary as well as in multicomponent mixtures. The method is extended to the real samples. The proposed method is simple, rapid, selective and reproducible.

A literature survey revealed that little information is available concerning the use of poly(dibenzo-18-crown-6) for the separation of gallium from other associated elements. We report herein a systematic investigation of adsorption chromatographic separation studies of gallium in hydrochloric acid medium.

Experimental

The apparatus and reagents used were similar as described in our earlier studies. The stock solution of gallium was prepared by dissolving pure gallium metal (0.5 g) (Johnson Matthey, UK) in hydrochloric acid (20 ml). The solution was made up to 250 ml with distilled deionised water. The solution was standardized complexometrically. The solution contained 2.07 mg/ml of gallium. The diluted solution containing 10 μg/ml of gallium was prepared by appropriate dilutions.

Procedure

An aliquot of sample solution containing 10 μg of gallium was mixed with hydrochloric acid in the concentration range 0.5-10.0 M in a total volume of 10 ml. The solution was then passed through the column, preconditioned with hydrochloric acid of the same acidity as that of the sample solution, at a flow rate of 0.5 ml/min. The column was washed subsequently with hydrochloric acid of the same acidity. The absorbed gallium was then eluted with different eluting agents (described later) at a flow rate of 0.5 ml/min. The 5 ml fractions were collected, after evaporating the acid from the effluent, the residue was extracted with water and the gallium content determined with 4-(2-pyridylazo)resorcinol (PAR) at 510 nm. The concentration of gallium(III) was computed from the calibration curve.

Results and discussion

Adsorption of gallium as a function of hydrochloric acid concentration on poly(DB-18-C-6)

An aliquot of gallium(III) (10 μg) was mixed with hydrochloric acid in the concentration range 0.5-10.0 M in a total volume of 10 ml. The solution was then passed through the column preconditioned with hydrochloric acid of the same acidity as that of the sample solution at a flow rate of 0.5 ml/min. Hydrochloric acid (0.1 M) was used as an eluting agent. It was observed that there was no adsorption of gallium at 0.5 M hydrochloric acid concentration. The adsorption started at 1.0 M (3%), was found to be 7% at 1.5 M and at 2 M (18%). The adsorption of gallium was 55% at 2.5 M and 80% at 3.0 M. Gallium was quantitatively adsorbed from 3.5-10.0 M hydrochloric acid concentration. Further adsorption studies of gallium(III) were carried out from 5.0 M hydrochloric acid.

Elution studies of gallium(III)

Gallium(III) was adsorbed on poly(DB-18-C-6) at 5 M hydrochloric acid concentration. After adsorption, gallium was eluted with various eluting agents such as hydrochloric acid, hydrobromic acid, perchloric acid, acetic acid, sulphuric acid in the concentration range 0.1-8 M.

The elution of gallium(III) was quantitative (100%) from 0.1-1.0 M hydrochloric acid. With 1.5 M hydrochloric acid, elution of gallium(III) was only 95%. The elution of gallium decreased with increase in HCl concentration and there was no elution of gallium from 4.0-8.0 M HCl. With hydrobromic acid, the elution of gallium(III) was quantitative from 0.1-2.5 M hydrobromic acid, from 3.0 M HBr concentration, elution of gallium(III) decreased. From 6.5-8.0 M hydrobromic acid, there was no elution of gallium. Perchloric acid, acetic acid and sulphuric acid were found to be the most efficient eluting agents for gallium(III). The elution of gallium(III) was quantitative with 0.1-8.0 M
perchloric acid, 0.1-7.0 M acetic acid and 0.1-8.0 M sulphuric acid. Further elution studies of gallium were carried out with 0.1 M hydrochloric acid.

The adsorption studies of gallium(III) were carried out on 1.0 g of poly(DB-18-C-6). The resin was preconditioned with 5.0 M hydrochloric acid. The concentration of gallium in feed solution was varied from 100-1100 μg/10 ml. Gallium(III) was eluted with 0.1 M hydrochloric acid and it was observed that the adsorption of gallium(III) was quantitative up to 680 μg/10 ml with a maximum of 98% at 700 μg/10 ml.

The capacity of poly(DB-18-C-6) for gallium(III) was found to be 0.932 mmol/g of crown polymer.

Separation of gallium(III) from binary mixtures
A solution containing 10 μg of gallium(III) was mixed with the foreign ions, to which hydrochloric acid was added so as to get a concentration of 5.0 M in a total volume of 10 ml. The tolerance limit was set as the amount of foreign ion required to cause ±2% error in the recovery of gallium. The binary mixture solution was then passed through poly(DB-18-C-6) resin column, preconditioned with 5.0 M hydrochloric acid, at a flow rate of 0.5 ml/min. Subsequently, the column was washed with 5.0 M hydrochloric acid. The foreign ions which were not adsorbed on poly(DB-18-C-6) resin column, passed through the column. The data revealed that amongst the alkali metals, sodium was adsorbed to the extent of 70%, potassium (80%) and rubidium (90%) whereas lithium and cesium were not adsorbed. Amongst alkaline earth metals, strontium and barium were adsorbed quantitatively. It was possible to separate a mixture of barium and gallium by eluting gallium with 8.0 M perchloric acid when barium remained in the column, which was then eluted with 1 M acetic acid. Most of the transition metal ions were not adsorbed hence passed through the column, except iron(III), molybdenum(VI) and uranium(VI) which were adsorbed quantitatively. The separation of gallium from iron(III) and molybdenum(VI) is described later. From p-block elements, only thallium(III) adsorbed quantitatively whose separation from indium and gallium is described later. Most of elements from s-block, p-block and d-block showed high tolerance limits. The anions of inorganic and organic acids also showed high tolerance limits.

Separation of gallium(III) from multicomponent mixture
When mixture containing gallium(III), indium(III) and thallium(III) was passed through poly(DB-18-C-6) column at 3.5 M hydrochloric acid concentration, gallium and thallium were adsorbed quantitatively whereas indium was not adsorbed when passed through the column. From the column, the adsorbed gallium was first eluted with 0.1 M hydrochloric acid, and then thallium was eluted with 1.0 M hydrochloric acid containing 20% acetone.

When mixture containing gallium(III), indium(III) and molybdenum(VI) was passed through poly(DB-18-C-6) column at 6.0 M hydrochloric acid concentration, indium(III) was not adsorbed when passed through the column whereas other elements were adsorbed. From the column, the adsorbed gallium was first eluted with 8.0 M perchloric acid, at this condition barium(II) and molybdenum(VI) remained in the column. Barium(II) was then eluted with 1 M acetic acid and finally molybdenum(VI) was eluted with 1.0 M ammonium hydroxide.

When a mixture containing aluminium(III), gallium(III), barium(II) and iron(III) was passed through poly(DB-18-C-6) column at 6.0 M hydrochloric acid, aluminium(III) was not adsorbed when passed through the column whereas all other elements were adsorbed. From the column, the adsorbed gallium and barium together were eluted with 7.0 M hydrochloric acid containing 1.0% TiCl₃. At this condition, iron(III) was not eluted, hence remained in the column which was then eluted with 1.0 M perchloric acid. The effluent containing the mixture of gallium and barium was then separated as described in the separation of binary mixtures. The separation of gallium(III) from other multicomponent mixtures were similarly accomplished.

Determination of gallium in real samples
Gallium was determined from rock samples such as Syenite rock SY-II, Basaltic rock BR and Nickel base alloy. The rock samples were opened and brought into solution as described elsewhere. A nickel base alloy (0.5 g) was treated with aqua regia and evaporated almost to dryness. It was then treated with 10 ml of conc. HCl and once again evaporated almost to dryness. The operation was repeated twice and finally it was extracted with distilled water.

An aliquot of a sample solution was then treated as per the general procedure. The separation of gallium, iron and other elements from the sample solution was carried out as described in the separation of gallium from multicomponent mixture. The results of triplicate analysis showed that the amount of gallium found in SY-II was 25.6 (26) ppm, in BR 20.4 (20) ppm and in nickel-base alloy it was 49.6 (50) ppm. The certified values are quoted in parentheses.
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References