

Anion exchange studies

XXIX. Adsorption of GeCl_4 from gas streams*

Germanium may be adsorbed from concentrated hydrochloric acid solutions by strong base quaternary amine anion exchange resins⁴⁻⁶. Unfortunately, under the conditions where Ge(IV) is effectively adsorbed, it is very volatile and hence there is considerable danger of losing significant amounts in analytical procedures involving anion exchange in HCl solutions. As described recently², this difficulty may be circumvented by operating in HCl-HF mixtures in which the volatility of Ge(IV) is low while conditions for good adsorption exist.

The high volatility of Ge(IV) in concentrated HCl solutions has often been used for analytical purposes⁷. The procedures normally involve distillation followed by

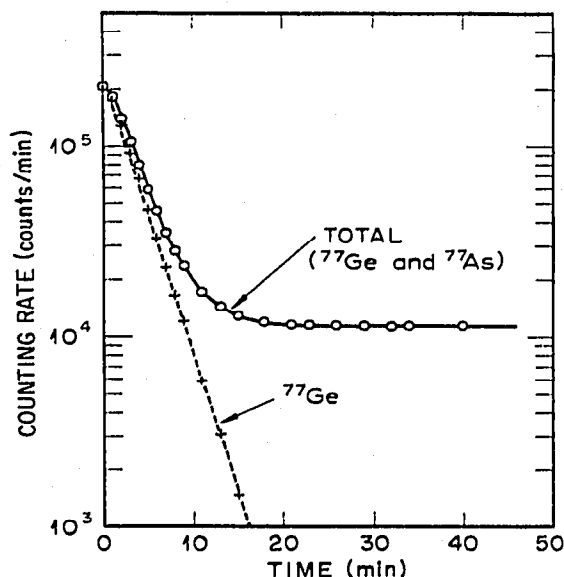


Fig. 1. Separation of ^{77}Ge from ^{77}As by gas-sweeping (12 *M* HCl, 25°).

condensation to recover Ge(IV). A high temperature gas-sweeping technique was used more recently to separate a short-lived isomer of Ge (^{73m}Ge , $T_{1/2} = 0.52$ sec) from its long-lived ^{73}As parent⁸.

It appeared that the analytical technique could be simplified (1) by using low temperature gas-sweeping techniques for removal of Ge(IV) from HCl solutions, and (2) by adsorbing Ge(IV) from the gas stream on an anion exchanger.

Low temperature gas sweeping permits essentially quantitative removal of Ge(IV) from concentrated HCl solutions as illustrated in Fig. 1. A 3 ml sample of

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12 *M* HCl containing ^{77}Ge tracer*, in secular equilibrium with its daughter ^{77}As , was placed in a small test tube fitted for gas sweeping with an inlet tube extending to the bottom of the test tube and with an outlet tube. The tube was placed in a well-type scintillation counter so that its counting rate could be followed continuously as nitrogen gas, previously washed with 12 *M* HCl, was passed through it.

The counting rate (corrected for "room" background) of the sample as a function of time is shown as a semi-log plot in Fig. 1. In this experiment a constant residual counting rate was reached in approximately 20 min. The remaining activity was found by radiochemical analysis to be ^{77}As . The rate of removal of ^{77}Ge , shown by the dashed

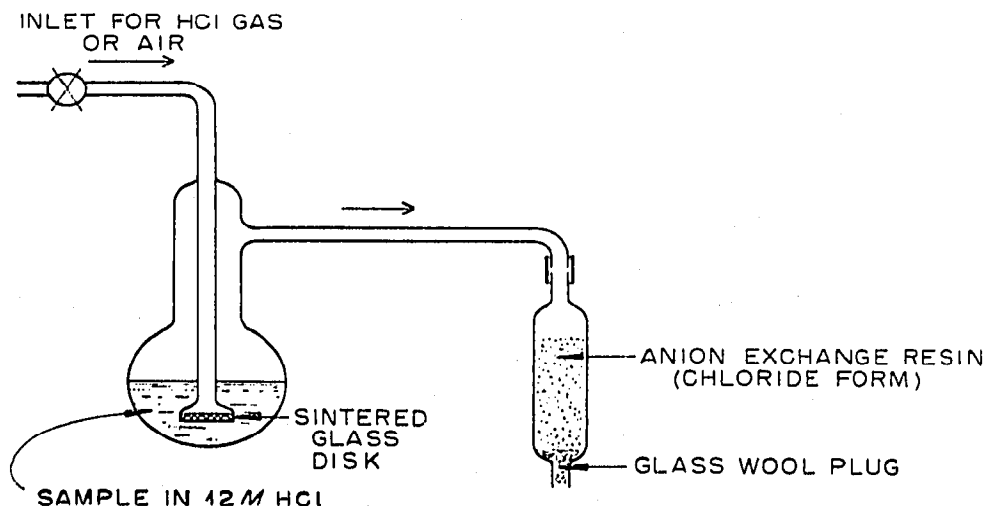


Fig. 2. Apparatus for distillation and adsorption of germanium.

line in Fig. 1, was obtained by correcting the observed counting rate for the ^{77}As background. The half-time of removal of Ge(IV) was *ca.* 2 min. which is sufficiently short for most analytical applications.

To test the effectiveness of anion exchange beds for removing Ge(IV) (GeCl_4) from HCl-rich gas streams, an apparatus similar to that illustrated in Fig. 2 was used. The sample containing ^{77}Ge in 12 *M* HCl was placed in a 5 ml distilling flask, connected by a side arm to two $0.25 \text{ cm}^2 \times 4 \text{ cm}$ beds of resin (Dowex-1 X 8, 50-100 mesh, capacity 3.4 moles per kg dry resin) arranged in series. The resin columns had previously been washed with distilled water and centrifuged for several minutes to remove most of the interstitial water. Nitrogen gas, washed with a large excess of 12 *M* HCl, was bubbled through the system at a moderate rate. After allowing sufficient time for quantitative removal of Ge(IV) from the solution (*ca.* 20 min) the columns were counted in a well-type counter. There was essentially quantitative adsorption of all Ge(IV) in the first column; no Ge-activity was detected in the second column.

Hydrochloric acid apparently is also strongly adsorbed from the gas stream by

* The tracer, ^{77}Ge - ^{77}As ($T_{1/2} = 12 \text{ h}$ and 40 h), was prepared by irradiating GeO_2 in the ORNL Low Intensity Test Reactor (LITR). The irradiated oxide was dissolved in 0.5 *M* NaOH to prepare a "stock" solution.

the anion exchange bed. This may readily be demonstrated by holding moist litmus paper in the exit gas stream or, more simply, by following a characteristic color change (yellow to amber) which this batch of resin shows on being saturated with HCl. Large amounts of HCl may be adsorbed by the ion exchanger and the frontal edge is sharp even with relatively rapid gas flow. With water-washed resins, the amount of HCl held was approximately 0.2 g per c.c. of bed corresponding to *ca.* 6 moles HCl per liter of bed.

If gas sweeping is continued until the resin column is saturated with HCl, there is danger of substantial loss of Ge(IV). For example, in one experiment gas sweeping was continued until the band of adsorbed HCl had reached the middle of the second column. Under these conditions *ca.* 20% of the ⁷⁷Ge activity was transferred to the second column and only 80% was retained by the first one.

One of the many advantages of the gas sweeping-anion exchange technique is the ease with which Ge(IV) may be recovered from the anion exchange columns. Desorption may readily be achieved by washing the columns with a few column volumes of water or, preferably, of dilute HCl solution. Since the first part of the effluent is rather concentrated in HCl, some care must be exercised to avoid loss of Ge(IV) by volatilization from the effluent.

The small scale technique described for separation and isolation of Ge(IV) should be adaptable to large scale applications provided precautions are taken to avoid complications resulting from the limited solubility of Ge(IV) in concentrated HCl solutions⁶ or in resin columns⁵.

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Plastic bag technique for paper chromatography

Conventional paper chromatography generally employs microgram quantities of the compounds to be separated per sheet of paper. Column chromatography is used for larger amounts. However, cellulose powder columns produce broader and not as well defined zones as separations on filter paper, which is more uniform in structure.

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