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UTILIZATION OF ISOTOPIC EXCHANGE FOR RADIOCHEMICAL SEPARATIONS

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SUMMARY

UTILIZATION OF ISOTOPIC EXCHANGE

FOR RADIOCHEMICAL SEPARATIONS

A rapid, high decontamination, single step method for separation of trace quantities of radioactive species such as silver and iodine has been developed. This method depends upon the rapid exchange between the ion and a thin film of solid silver halide supported on a platinum gauze electrode. High yields of the radioactivity are obtained in a few minutes. Effects on the yield of time, temperature, amount of precipitate, foreign salts, etc., have been studied. Decontaminations (some as high as 10^6) have been determined with tracers of 16 typical elements.

By utilizing columns with plates or beads of metal coated with such a precipitate, this method might take its place beside standard engineering operations such as distillation, ion exchange, etc., for trace separation of radioisotopes of a number of elements.

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Introduction

The problems of analytical control for chemical process systems in the atomic energy industry are often very similar to those of the chemical processes themselves. Very high decontaminations are required for both types of separations. Hence precipitation procedures have, in many cases, given way to the more highly decontaminating techniques of ion exchange or solvent extraction. Batch ion exchange procedures are not very specific and use must be made of column techniques to achieve satisfactory separations. These techniques, however, result in low flow rates and hence low thru-put for separations involving similar elements. Liquid-liquid extraction may, on the other hand, be quite specific in certain cases when solution composition is closely controlled. The mechanical contacting of two liquid phases leads, however, to occlusion and incomplete phase separation, requiring a number of scrub stages to approach the theoretical capabilities of the method. One further requirement of all methods is that of rapidity of operation whether for the control laboratory or the processing plant.

Existing procedures are not completely satisfactory on a number of these counts and hence we have initiated a program of critical evaluation of radiochemical separations. Separations listed in the literature for one element (or a group of elements) are checked to find several of the most promising. These procedures are then subjected to a large number of exhaustive tests to determine optimum conditions, interference effects of macro amounts of foreign ions, and the actual decontamination values for some sixteen different typical tracer elements.

An early result of this evaluation program was the application (2) of the technique of isotopic exchange to radiochemical separations. This is a technique which is particularly well suited to radiochemical work since it is highly specific, is very rapid, gives very high decontaminations in one step, and suffers few interferences. Thus the procedure requires few solution adjustments, and is readily adaptable to remote handling.

A. Langer (1) of the Westinghouse Research Laboratories in 1942 studied, with the help of a radioactive tracer for silver, the exchange of silver ions between freshly precipitated silver chloride and a solution of silver nitrate. He found the exchange to occur rapidly and to be a predictable function of the temperature. At equilibrium, the distribution of any given isotope of silver between the solid halide and the solution is determined by the relative weights of silver in the solid halide and in the solution. For example, if 1 mg of radioactive silver-110 in solution is equilibrated with solid silver chloride containing 100 mg of silver, none of which

is silver-110, the ratio of silver-110 in the solid to that in the solution at equilibrium will be 100:1. If the ratio of these initial weights is much larger than 100:1, as would be the case if only trace amounts of silver-110 existed in the solution and if all the inactive silver were in the form of the solid halide, then the ratio at equilibrium will be correspondingly larger, giving an even better separation yield than the 99% value in the example given above. We have applied this principle to the problem of separating radioactive silver from other activities and also have obtained preliminary information on the separation of iodine by this method.

General Experimental Procedure

Silver metal is deposited electrolytically from a cyanide solution onto a platinum gauze. It is then electrolyzed as the anode in dilute hydrochloric acid solution to convert the silver to silver chloride and, finally, this electrode is contacted with an acid solution containing trace amounts of radioactive silver. After a suitable contact period, the gauze is removed, washed, and counted in a well-type scintillation counter to determine the extent of exchange. For the separation of iodine, a silver iodide electrode is prepared in a similar manner. Iodine solutions containing radioactive iodine are then contacted with the electrode and the exchange assayed with the well counter. For more accurate assay work, the halide surfaces containing the tracer are dissolved from the gauze, reprecipitated and counted in a more reproducible geometry than can be obtained by counting the halide on the gauze.

This method was found to give a very rapid separation of silver. With efficient stirring, about 97% of the radioactive tracer was removed in five minutes at room temperature from a solution 1 M in HNO_3. About 98% of the silver was removed in two minutes from a similar solution at 95°C. For iodine, the separation is less rapid and in many cases incomplete, even after a contact time of 1 hour. Between 65 and 80% of the iodine-131 is removed from solution under the conditions described above in a period of 5-15 minutes. Higher yields require the use of a second gauze.

Silver Separation

For the removal of silver, the method was found to be "quantitative" within the counting error when reproducible standardized conditions were used. For this quantitative procedure 10 mg of silver was plated on the platinum gauze and a 15 minute contact time used with the active solution. For high decontamination work this was followed by a 1.5 minute wash with 1:1 HNO_3. The results of a series of analyses using this method gave an average yield of 99.3 $\pm$ 0.7% (standard deviation). No decrease in yield is observed with gauzes which are prepared one week before use and stored in 1:1 HNO_3.

This method was found to suffer little interference from other ions often found in radioactive mixtures. Nitrate solutions of bismuth, aluminum, copper and zinc showed no interference (loss in yield of the silver tracer)

in concentrations less than 1 M. Acids such as nitric, hydrochloric and hydrofluoric do not interfere in concentrations less than 2-3 M, and sulfuric acid does not interfere below 1.5 M. These results indicate that the interference is due to the anion concentration rather than to specific cationic interferences. This may be due to the formation of an anionic layer on the halide surface which restricts the mobility of the silver in the vicinity of this surface.

Sixteen different radioactive species were studied to determine the level of decontamination which could be expected from this procedure. The elements studied fall into two categories; those with decontamination factors greater than 10^6, and those with decontamination factors between 10^3 and 10^5, for a single contact step of 15 minutes. In the first group are the alkaline earths, alkali metals and rare earths. Seven elements were studied in this group. In the second group appear the elements which readily form complexes such as tin, antimony, zirconium, niobium, tantalum, iridium, ruthenium and cobalt. Contamination of the gauze by these elements may be due to the formation of compounds between the silver on the halide surface and the complexes of the trace elements in solution. If this were the case, the contamination would be lowered as one progressed from chloride to bromide to iodide surfaces. This reduction of contamination was demonstrated experimentally for radioactive ruthenium-106.

Applications

The rapidity of the method is a particular advantage in the radiochemical laboratory. It is even suitable for the separation of short-lived silver isotopes such as the 2.3-minute silver-108. When yields are not of primary importance, 50% of the silver can be removed from solution in just 20 seconds at 95°C.

The high decontamination afforded by the procedure is due to the inherent specificity of the isotopic exchange reaction itself. A contribution is made to this decontamination by the fact that a large mass transfer is not involved in the separation. The techniques of precipitation, electrodeposition, distillation and to some extent ion exchange are limited in separation efficiency by the fact that a large mass transfer promotes occlusion, coprecipitation, and entrainment. The technique of isotopic exchange has the lowest mass transfer and hence the possibility for high decontamination in a single step.

The insensitivity of the method to changes in acid and salt concentration necessitates fewer solution adjustments prior to the separation step and hence lessens the possibility of hydrolysis or radiocolloid formation.

This separation technique should prove very useful for the production of radioisotopes. Silver-110 and silver-111 samples could be readily separated from bombardment or fission product mixtures even in the multi-curie region. Iodine-131 could also be readily separated in multi-curie lots of high specific activity. The procedure cannot, however, produce iodine "carrier free." Furthermore, contact with several electrodes or use of a column technique might be required for total recovery.

Silver-111 separated by this method from neutron irradiated palladium is ideal for making intense beta-ray sources. The radioactive silver chloride can be dissolved from the platinum gauze after contact and silver electrolyzed on an electrode of any desired shape or form.

The simplicity of the operations involved in this procedure allow its adaptation to remote handling of high radiation levels. Many of the possible contamination problems involved in other types of systems are thus eliminated.

The method described above uses strictly a single contact system. If a multiple contact system were devised, the decontamination should be even more striking. This might be accomplished by packing a column with plates or beads coated with a silver halide for either silver or iodide separations. The softness of the silver halide coating might limit the use of this method however. Further advancement in these techniques may well give this method a place beside standard engineering operations such a distillation, ion exchange, etc.

To date, separations of this type have been made only on the silver halides. The work may possibly be extended to a number of other elements exhibiting rapid exchange between a solid and the ion in solution.

References

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