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RADIOCHEMICAL SEPARATIONS BY ISOTOPIC EXCHANGE:
A RAPID, HIGH DECONTAMINATION METHOD FOR SILVER

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RADIOCHEMICAL SEPARATIONS BY ISOTOPIC EXCHANGE:

A RAPID, HIGH DECONTAMINATION METHOD FOR SILVER[1]

It has been reported by Langer[2] that the exchange of silver ion between a precipitate of silver chloride and a solution of silver nitrate reaches isotopic equilibrium very rapidly. Because of the low solubility of silver chloride, a very favorable ratio exists at equilibrium between the silver atoms in the precipitate and the silver atoms in the solution. For this reason if silver chloride is added to a solution containing only trace amounts of radioactive silver, a high percentage of this silver will have exchanged with the silver in the precipitate by the time equilibrium is attained. Use has been made of this fact to develop a rapid, high decontamination, single step method for the separation of traces of radioactive silver from a solution containing other radioactive species.

Platinum gauze about 1 1/4" high and 3/8" in diameter is coated with metallic silver by plating from 10 ml. of solution containing 10 mg. of silver as the nitrate in 3 M NaCN and 0.5 M NaOH. The plating process requires about 4 minutes at 3 volts[3], and results in the deposition of about 5 mg. of silver. The electrode is washed with water for 30 seconds and immersed in 10 ml. of 0.05 M HCl. The current is then reversed, the silver surface used as the anode, and electrolysed at 1 1/2 volts for about 15 minutes, changing the silver to silver chloride. The finished electrode is washed and can be stored in 1-1 HNO_3 for at least 24 hours before use.

To separate radioactive silver from other activities (except halides), the "silver chloride electrode" is immersed for 5 minutes at room temperature in about 10 ml. of an acid solution containing the active material. The solution may be stirred magnetically. The electrode is removed and washed with a stream of 1-1 HNO_3 for one minute. This thorough wash is essential when high decontaminations are required. The one minute wash decreased the contamination from other activities by a factor of four over that obtained after a half minute wash. Further washing failed to further decrease this contamination.

Yields of radioactive silver from this procedure are given in Table I for varying temperatures, amounts of silver chloride and times of immersion. The exchange rate appears to be independent of the nitric acid concentration in the range of 0.1 to 4 M , while at 8 M HNO_3 only 92% and at 16 M HNO_3 only 50% is exchanged in 5 minutes at 25°C. The exchange is also independent of hydrochloric acid concentration in the range 0 to 0.6 M, while in 1.2 M HCl only 77% and in 6.0 M HCl only 30% of the silver is exchanged in 5 minutes at 25°C. This effect of HCl is noted only so long as the silver concentration is so low that the solubility product of silver chloride is not exceeded in the tracer solution before immersion of the electrode. Higher concentrations of silver were not studied with hydrochloric acid.

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(2) A. Langer, J. Chem. Phys., 10, 321 (1942).

(3) An inexpensive battery eliminator (Model BE-4) available from Heath Company, Benton Harbor, Michigan is used as a source of direct current and the voltage indicated is that appearing on the built-in voltmeter.

The decontamination afforded by this method was studied in three ways. First, a solution containing 10^6 disintegrations per minute of four year old fission products was contacted with the "silver chloride gauze" for five minutes at 25°C. Of the 540 d/m detected on this gauze, 500 d/m were proven to be due to silver isotopes. Silver was determined by a procedure involving silver chloride precipitation, dissolution in ammonia, reprecipitation with nitric acid, dissolution in sodium cyanide and electrolysis of the resulting solution. A freshly prepared "silver chloride gauze" was then immersed in the same solution of fission products from which the silver had been removed. The 42 d/m of activity found on the gauze after washing indicated a decontamination of about 2×10^4. The activity was determined by counting the entire gauze in a well type scintillation counter.

Next, a sample of cadmium metal wrapped in aluminum foil was bombarded with deuterons in the University of Michigan cyclotron. This bombardment produces roughly 10^3 more radioactive atoms of indium and cadmium than of silver. The metal target was dissolved in a mixture of nitric acid and hydrofluoric acids and the "silver chloride gauze" was immersed for three minutes in this warm solution. Upon removal, the electrode was washed for one minute with 1-1 HNO_3 and the decay of the silver isotopes followed with the scintillation well counter and four-pi beta proportional counter. The decay curves obtained were identical with those obtained previously with silver separated from targets of this type by means of several cycles of silver chloride precipitations with HCl, and dissolutions with ammonia.

In the third case, contamination of the "silver chloride gauze" by iodine was studied with iodine of high specific activity obtained from Oak Ridge National Laboratory. Prior treatment of the iodine solution with fuming nitric acid, sodium bisulfite, or sodium nitrite to adjust its oxidation state to a point where the iodine either gave no interference or was carried quantitatively, gave results that were neither quantitative nor reproducible. However, warming 0.1 ml. of the iodine solution for 15 seconds with a mixture of 1/2 ml. 1 M $KMnO_4$ and 1/2 ml. 16 M HNO_3 produced a solution which upon dilution to 10 ml. did not exchange appreciably with the silver chloride. Immersion of a "silver chloride gauze" in an iodine solution prepared in this manner removed only 1 part in 10^4 of the iodine activity present. On the other hand, the silver exchange is less rapid in this solution, giving 85% exchange in 5 minutes at room temperature and requiring 20 minutes for greater than 98% recovery.

The advantages of this exchange method include its rapidity and high decontamination in a single step. For example at 95°C a 50% recovery is possible in only 20 seconds as shown in Table I. The rapidity of this exchange as suggested by Langer is apparently due to the high mobility of silver ions within the crystal lattice of silver chloride as well as from the solution to the solid. The high decontamination from other activities is due to the specificity of the exchange reaction and the simplicity of the manipulations. It involves only immersion of solid silver chloride in a compact form, stirring the solution, and washing the electrode at completion. No precipitate is formed within the solution, no reagents are added except solid silver chloride, and in most cases no adjustment of acidity is necessary. Greater than 98% recovery is possible as long as the weight of solid inactive silver chloride is at least 50 times the weight of tracer silver in the solution.

Table I. Yields of radioactive silver from 1 $\underline{M}$ HNO_3 by exchange procedure.

Mg. AgCl	Immersion Time	Temp.	% Recovery
2	5 min.	25°C	> 97%
2	2 min.	95°C	> 98%
2	20 sec.	95°C	50%
0.3	5 min.	25°C	85-90%

We believe this method will find use in radiochemical separations where speed is required and where the yields need not be quantative. The method should prove useful in the rapid preparation of high specific activity silver from irradiated materials such as palladium and also in the rapid determination of silver in fission products. It is also readily adaptable to work with high levels of radiation where handling by remote control is necessary.

This exchange method of radiochemical separation appears to have general applicability and should prove useful for separations of other elements displaying rapid exchange between phases.