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RADIOCHEMICAL SEPARATIONS: II.
SEPARATION OF RADIOACTIVE SILVER BY ISOTOPIC EXCHANGE

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RADIOCHEMICAL SEPARATIONS: II. SEPARATION OF RADIOACTIVE SILVER
BY ISOTOPIC EXCHANGE

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ABSTRACT

The principle of isotopic exchange has been adapted to the separation and determination of radioactive silver from a mixture of radioactive species, and a quantitative procedure developed.

The separation of radioactive silver by isotopic exchange with a silver chloride surface was found to be quantitative in fifteen minutes or less, even in the presence of high concentrations of many inorganic salts and organic solvents. The method is quite specific for silver, with decontamination factors between 10^3 and 10^7 for eighteen representative radioactive species. The method was also applied to the separation of silver from fission products and bombardment samples and found satisfactory in both cases.

INTRODUCTION

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.

By use of the technique of isotopic exchange (6, 7) it is possible to shorten existing procedures for the separation of silver without sacrificing specificity or yield. Isotopic exchange involving silver halides and silver salts in solution has been studied by Langer (2, 3) and in one case was applied to the determination of macro amounts of silver (4). This method has also been applied to the preparation of beta-ray sources (5), and the separation of I-131 (9). A method for the separation of iodine on a base material of AgCl recently reported in the literature (1) is based upon elemental substitution of chloride for iodide by the silver chloride rather than isotopic exchange.

APPARATUS AND REAGENTS

Apparatus

International Clinical Centrifuge,
Scintillation well counter, Nuclear Instrument and Chemical Corporation, Model DS-3 with 2 in. additional lead shield.
Scaler, Nuclear Instrument and Chemical Corporation, Model 162, scale of 12^8 , modified to count with preset time and preset count and to reset automatically.
Battery Eliminator, Heathkit Model BE-4, Heath Company, Benton Harbor, Michigan.
Magnetic Stirrer, manufactured by G. F. Smith Chemical Company, Columbus, Ohio.
Platinum Electrodes, 10 mm diameter, 30 mm high, 52 mesh, manufactured by American Platinum Works, Newark, New Jersey.

Reagents

Sodium Cyanide, (Mallinckrodt Reagent No. 7616), 3 M.
Sodium Hydroxide, (Mallinckrodt reagent No. 7680), 5 M.
Hydrochloric Acid, concentrated, (B and A reagent No. 1090).
Nitric Acid, concentrated, (B and A reagent No. 1120).
Sulfuric Acid, concentrated, (B and A reagent No. 1180).
Hydrobromic Acid, 48%, (B and A reagent No. 1085).
Hydriodic Acid, sp gr 1.5, (Merck reagent No. 0246).
Hydrofluoric Acid, 48%, (B and A reagent No. 1100).
Acetic Acid, glacial, (B and A reagent No. 1019).
Aluminum nitrate, (Mallinckrodt reagent No. 3172).

Bismuth nitrate, (B and A reagent No. 1456).

Cupric nitrate, (B and A reagent No. 1641).

Ferric nitrate, (B and A reagent No. 1739).

Sodium acetate, (B and A reagent No. 2191).

Zinc nitrate, (B and A reagent No. 2445).

Radioactive Tracers: Obtained from the Isotope Control Division of Oak Ridge National Laboratory and used without added carrier. Nuclear and chemical characteristics of these tracers are tabulated in the first paper of this series (8).

EXPERIMENTAL PROCEDURE

A silver chloride electrode of large surface area is made from an electrode of fifty-two mesh platinum gauze, ten mm in diameter and thirty mm high. Ten mg of silver metal is deposited on the gauze by electrolysis for ten minutes at four volts from ten ml of a solution three M in NaCN and 0.5 M in NaOH. A simple battery eliminator was used as a source of voltage for these experiments. The whitish surface of silver metal is rinsed with water, inserted in ten ml of 0.05 M HCl and electrolyzed as the anode for five minutes at one volt, completely converting the silver metal to silver chloride. The electrode is washed with eight M HNO₃ and is ready for use.

To separate silver by isotopic exchange, the silver chloride electrode is contacted with ten ml of solution containing a very low concentration of radioactive silver. The solution is stirred magnetically. The gauze is then removed from the solution and washed with eight M HNO₃ for one minute. It is rinsed with acetone, placed in a lusteroid cone and counted in the scintillation well counter. If quantitative counting and recovery of the silver is desired, the silver chloride may be dissolved in ammonium hydroxide, acidified, and the silver chloride precipitate separated by centrifugation or filtration and mounted for counting.

The standard method referred to hereafter as the "quantitative procedure" for separating trace silver requires the use of ten mg of silver as silver chloride on the electrode and fifteen-minute contact with the tracer solution one M in HNO₃ at room temperature. The silver chloride is then dissolved, transferred to a culture tube, reprecipitated, centrifuged, the supernate removed and the precipitate counted in the scintillation well counter.

RESULTS AND DISCUSSION

Yields of Silver

Recovery of silver tracer in the quantitative procedure using ten mg, four mg and one mg of silver as AgCl on the gauze are given in Table I. For each determination 20,000-40,000 d/m of Ag-110 tracer was used. All samples were counted to a probable error of 0.4%. Errors quoted in the table are standard deviations.

Table I

Yield of Radioactive Silver by Exchange
with Silver Chloride

Deter- mination	Weight of Silver on Gauze		
	10 mg (%)	4 mg (%)	1 mg (%)
1	99.5	99.0	93.0
2	98.5	99.1	94.3
3	99.8	98.8	94.7
4	99.8	99.0	94.9
5	99.8	98.8	95.8
6	99.2	99.0	
7	100.0	98.7	
Avg. and Std. De- viation	99.5 \pm 0.5	98.9 \pm 0.2	94.5 \pm 1.0

The silver chloride surface prepared in the manner described above is not ideal from the point of view of mechanical stability. During the course of the procedure a rather small amount of silver chloride is lost, due apparently to chipping or chalking of the electrode surface in the contacting and washing periods. Experiments indicate that this

chalking loss is of the order of 0.05 mg of silver chloride. Thus if only one mg of the chloride precipitate is used originally, this loss is an appreciable portion of the total while it is negligible in the ten mg samples used routinely.

As noted in Table I, however, reproducible results can be obtained with four mg and even one mg amounts of silver. Thus it is possible to use such small amounts if, because of self-absorption or other considerations, it is necessary to obtain a high specific activity.

Fifteen minutes contact time under ideal conditions is more than sufficient for complete removal of the radioactive silver from solution, as shown in a later section. Actually at 25°C the 97% removal point occurs at five minutes and over 99% is obtained in six to seven minutes. This range of five to seven minutes, however, is a very sensitive one as far as interfering ions and nonideal conditions are concerned. Thus the fifteen minute time was chosen to minimize the effect of small changes in acidity, stirring, and the character of the silver chloride deposit.

The one-minute wash of the silver chloride gauze after exchange is necessary where decontamination from other activities by a factor of 10^6 is desired. Washing for a longer period of time had no effect. Eight M HNO₃ proved effective as the wash solution for all the contaminating activities used in this work. If other conditions warrant their use, even organic wash solutions could be applied.

It was found essential to dissolve the silver chloride surface and reprecipitate it for the quantitative recovery of radioactive silver and its reduction to a reproducible form for counting. This was necessary because it was impossible to reproduce counts of the gauze to better than 2-3%.

When very small amounts of inactive silver are desired on the gauze, the lower limit appears to be dependent upon the manipulatory techniques in making the silver plate on the gauze. This means first that the more uniform the deposit, the more area is made available for exchange for a given small amount of silver. Secondly, silver in sub-milligram amounts is perhaps dissolved or in any case lost from the electrode in the process of removing it from the cyanide solution. This is shown by the graph in Fig. 1 in which the time of electrolysis is plotted against the fraction of metallic silver deposited on the platinum gauze from cyanide solution using the standard four-volt cell and varying the amount of silver in solution. Silver-110 was used as the tracer to follow the deposition in these experiments.

Silver iodide surfaces are also quite suitable for the exchange separation of tracer silver. The rate of exchange is not significantly different than that with silver chloride in that 97% is removed in six minutes and 99% in nine minutes with ten mg silver as AgI. In some cases, the iodide may be considerably better for exchange purposes due to its lower solubility, but further separations are often complicated by the presence of the active silver in the form of the difficulty soluble iodide. One method used in this laboratory to by-pass these difficulties was to electrolyze the "AgI gauze" containing the tracer silver as cathode in a neutral conducting solution such as sodium acetate for one minute at a voltage sufficient to decompose the silver iodide. The iodide ion goes into solution and free silver remains as a black deposit on the electrode. This free silver may then be dissolved in nitric acid.

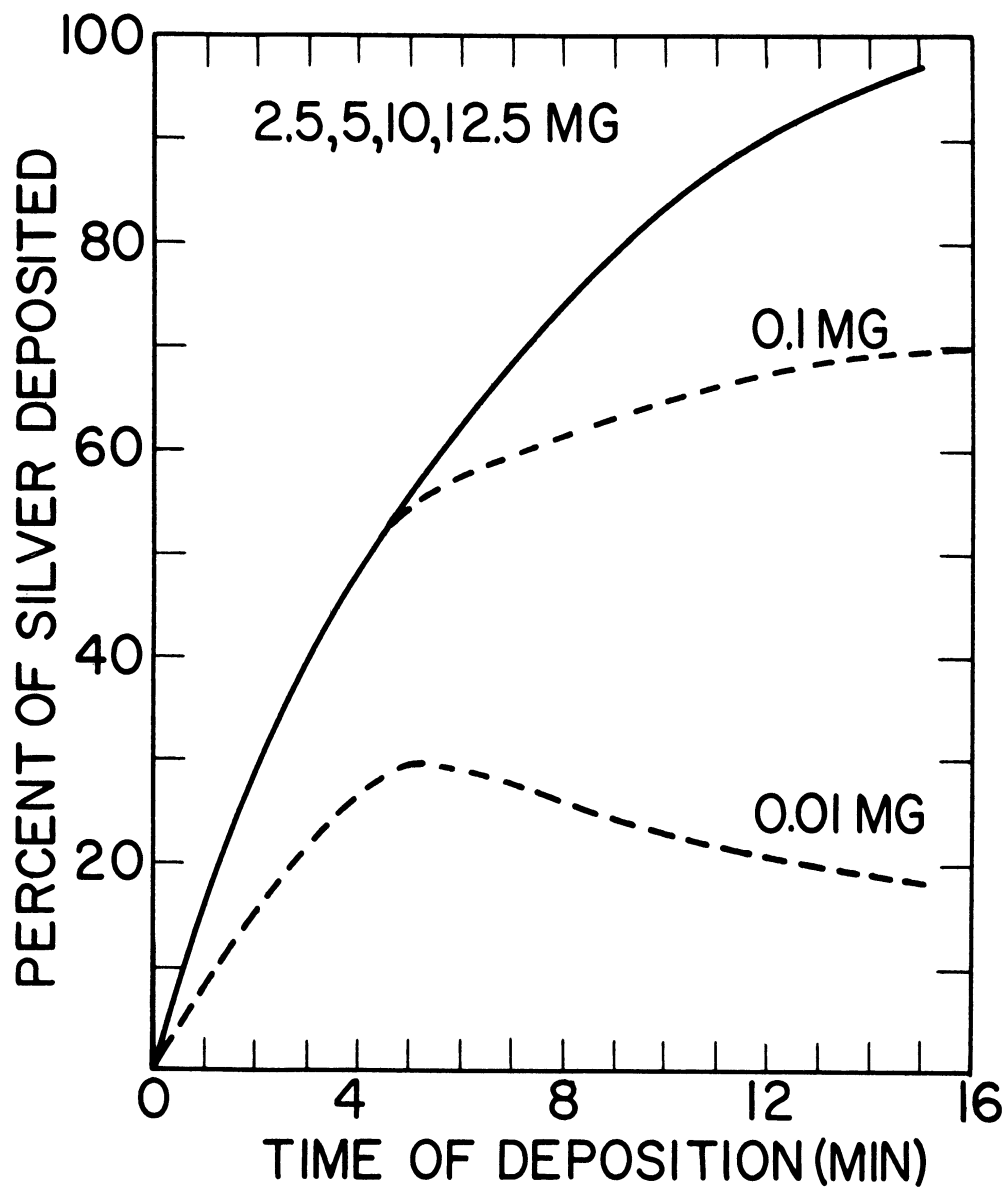


Fig. 1.

Influence of Total Amount of Silver Present on the Yield of Silver Deposited Electrolytically from a Cyanide Solution.

Contamination

The quantitative procedure was checked with eighteen different representative tracers to determine the levels of contamination which might be expected. Long-lived daughter activities of the tracers were also considered since no carriers were present and no attempt was made to separate parents from daughters. In these experiments the only radioactivity present was that of the element being studied. The contamination of the AgCl gauze by each element is given in Table II. All results are an average of at least two determinations.

Table II
Contamination of Silver by Other Activities
in Isotopic Exchange Method

Activity	Percentage Carried on Gauze
Ba-140, La-140	0.00005
Ce-144, Pr-144	0.0001
Cs-134	0.0001
Co-60	0.001-0.0001
Cr-51	0.01
I-131	0.01-0.001
Ir-192	0.1-0.01
Ru-106, Rh-106	0.1
Sb-124	0.01
Se-75	0.1
Sn-113, In-113	0.1-0.01
Sr-90, Y-90	0.0001
Ta-182	0.01
Zr-95, Nb-95	0.01-0.001

To obtain more information concerning the mechanism of contamination of the AgCl gauze by foreign activities it is advantageous to arrange the data in the form of Table III illustrating the similarity of those activities giving the largest contamination.

Table III
Contamination Summary

	Percentage Carried	Elements
Group A	0.1-0.001	Cr, I, Ir, Ru-Rh, Sb, Se, Sn-In, Ta, Zr-Nb
Group B	0.00.-0.00001	Ba-La, Ce-Pr, Co, Cs, Sr-Y

The elements in Group A which show some tendency to contaminate are those elements which in general, form very strong halide complexes with chloride and fluoride. (The iodide case is different in that about 10% of the tracer iodide is carried on a silver chloride gauze after a fifteen-minute contact. The 0.01% figure of Table II for iodine is obtained after treatment of the I-131 solution with HNO₃ and KMnO₄ to oxidize the iodide to iodate. The iodate is more soluble than the iodide and the chloride by factors of 10⁴ and 10² respectively so it would not be expected to replace either of them on the gauze surface.) The contamination of the gauze by the complex formers may be by adsorption of chloride complexes of the individual elements on the silver chloride surface. Perhaps these complexes actually replace the silver chloride with insoluble compounds of the type Ag₂IrCl₆, similar to the slightly soluble Cs₂PtCl₆ or even Ag₄Fe(CN)₆.

If this explanation were correct, a less soluble surface such as AgBr should reduce contamination and a AgI surface should reduce it even further. The degree of Ru-Rh contamination of AgBr and AgI surfaces was studied to determine whether this were the case. These results along with the corresponding AgCl data are shown in Table IV and indicate that the availability of silver ions or halide ions or both does indeed influence the contamination by this particular activity.

Table IV
Contamination of Silver Halide Surfaces
by Ru-Rh Tracer

Surface Material	Percentage of Ru-Rh Activity Carried
AgCl	0.1
AgBr	0.04
AgI	0.003

In the cases of zirconium-niobium and tantalum activities, the contamination is probably due to hydrolytic effects such as radio-colloid formation or adsorption of basic salts.

Three more general determinations of decontamination were made with this procedure. First, the silver chloride gauze was contacted with a solution containing four-year-old fission products in unseparated form. After a fifteen-minute contact, 0.001% of the fission product activity was found on the gauze. In the second determination, cadmium metal was bombarded with deuterons in the University of Michigan cyclotron, the target was dissolved in nitric and hydrofluoric acids and the silver produced by the (d, α) reaction removed by isotopic exchange. Due to the rapidity

of the separation it was possible to detect a two-minute silver isotope which was never seen when precipitation separations were used. The decay was followed in the scintillation well counter as well as a four-pi beta proportional counter and the decay curves showed as clean a separation from cadmium and indium activities as had a series of precipitation separations requiring forty-five minutes. For the third determination a Pd-109 irradiated unit, containing about 300 mc of thirteen hr Pd activity and 2-3 mc of Ag-111 with a 7.5 day half-life, was obtained from Oak Ridge National Laboratory. The palladium was dissolved in aqua regia, diluted to a four M HNO₃ solution and the silver removed by isotopic exchange. The AgCl gauze obtained weighed ten mg and contained two mc of Ag-111 which gave a reading of three "r/hr" at six inches when monitored. Its decay was followed in the scintillation well counter and the GM end-window counter. The semilog plot of the decay was linear over more than five half-lives and no other activity was detected.

Interferences

A study was made of the effects of inactive species present in varying concentrations and forms in the solution from which tracer silver is to be removed. About 40,000 d/m of Ag-110 were added to solutions containing the given concentration of interfering specie, the quantitative procedure used to remove the silver activity, and the yield determined. The species chosen were those which were considered to be of most interest, with the greatest likelihood of appearance in process solutions. The values for the silver tracer yield are given in Table V.

This study of the effect of inactive species in high concentrations revealed few specific interferences. The only substance which

Table V

Effect of Interfering Substances upon Exchange
of Silver with Silver Chloride

Specie	Concentration	Percentage Yield of Ag-110
HNO ₃	1 <u>M</u>	99
	4	99
	8	93
	12	91
	16	85
HCl	0.05 <u>M</u>	98
	0.5	99
	1.0	98
	3	89
	6	41
H ₂ SO ₄	1.5 <u>M</u>	97
	3	90
	6	79
HF	1.1 <u>M</u>	98
	3.3	98
	6.6	83
	13.2	57
	22	18
HC ₂ H ₃ O ₂	99%	42
Al(NO ₃) ₃	2 <u>M</u>	86
	1	95
	0.5	99
Cu(NO ₃) ₂	2 <u>M</u>	95
	1	97
	0.5	98
Zn(NO ₃) ₂	2 <u>M</u>	95
	1	97
Fe(NO ₃) ₃	2 <u>M</u>	94
	1	93
	0.5	95
Bi(NO ₃) ₃	2 <u>M</u>	93
	1	97
	0.5	100

Table V (cont.)

Specie	Concentration	Percentage Yield of Ag-110
NaC ₂ H ₃ O ₂	2 M	95
	1 M	97
	0.5	98
C ₂ H ₅ OH	99%	36
	50	95
	25	98
(CH ₃) ₂ CO	99%	70
	50	95
	25	98

showed adverse effect on the yield of tracer silver was Fe(NO₃)₃. Yield values remained between 93 and 95% for this compound. For other salts and acids included in the study, the effect seems to be one of salt concentration rather than a specific effect of any individual ion or salt. In Table VI the anionic molarity of each salt is listed opposite the concentration at which that salt first resulted in less than 97% yield of the tracer silver. In this work the AgCl gauzes were counted with an accompanying error of 2-3% as explained earlier.

Table VI
Interference Summary

Specie	Anionic Molarity at Critical Concentration
HNO ₃	4-8 M
HCl	1-3 M
H ₂ SO ₄	1.5-3
HF	3-6
Al(NO ₃) ₃	3
Bi(NO ₃) ₃	3-6
Cu(NO ₃) ₂	4
Zn(NO ₃) ₂	4
NaC ₂ H ₃ O ₂	2

It would appear from these data that a concentration of anion of greater than $2 \cdot 10^{-8}$ M, depending upon whether it is nitrate, chloride, sulfate, fluoride or acetate, will result in losses of silver under the procedures used. A look at the mechanism of the separation may show the reason for this concentration effect. Silver chloride, as freshly precipitated, is well known for its ability to adsorb either positively or negatively charged ions, depending upon which is in excess. Use is made of this fact by the Fajans method for determination of end point in the titration of chloride with silver nitrate, by use of dichlorofluorescein. To effect the isotopic exchange which is required for separation, high ionic mobility is required in the immediate vicinity of the silver chloride surface. A stable ionic layer adjacent to the exchanging surface might lower this mobility and cause loss of yield. Cognizance should be taken of this possibility before adoption of this method for highly salted solutions.

The effect of the two aqueous-organic systems studied indicates that minor concentrations of either acetone or ethyl alcohol will not prevent quantitative removal of silver tracer since they apparently have no specific deactivating effect on the AgCl surface. "AgCl gauzes" did, however, show lower activity toward exchange if they had been rinsed with acetone and dried prior to exchange.

Dependence of Yield on Time and Temperature

If for any reason fifteen minutes is too long a contacting time, shorter periods can be used. Experimental determinations of the extent of exchange for a number of temperatures are plotted against time in Fig. 2. As would be expected, the exchange is more rapid at the higher temperatures.

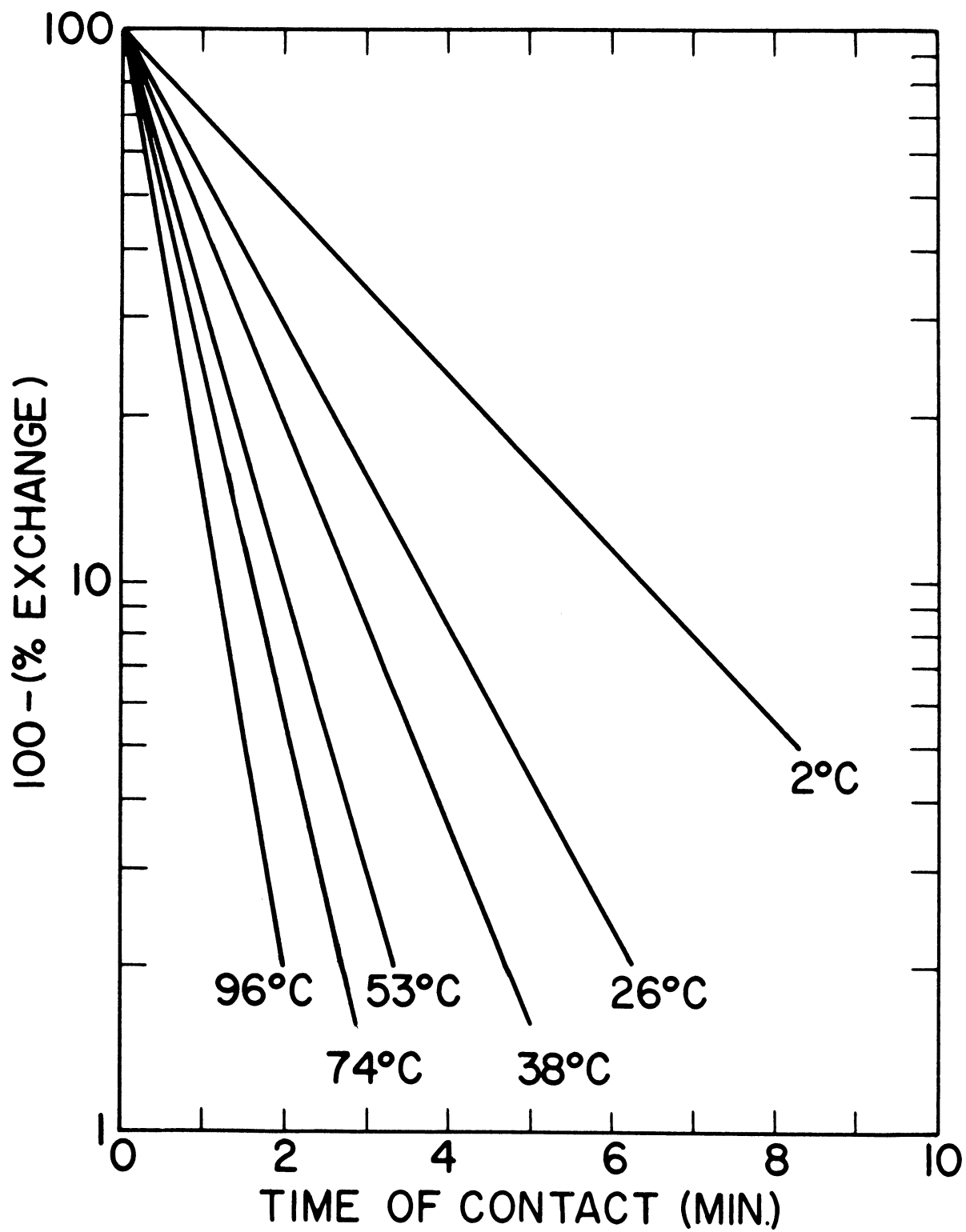


Fig. 2.

Temperature Dependence of Rate of Exchange
of Silver Ion with Silver Chloride.

It can be seen from this temperature dependence that considerable time economies can be realized by raising the temperature of the contacting solutions. At 96°C, for example, over 95% of the tracer can be separated with only two-minute contact, the 50% point being reached in twenty seconds. Use was made of this fact to separate silver with sufficient rapidity to measure the rate of decay of a two-minute isotope formed by the (d, α) reaction on cadmium.

Aging of Silver Chloride

Most of the work described above was carried out with AgCl gauzes prepared within one hour of use. Because of the light sensitivity of AgCl and the fact that isotopic exchange must necessarily occur on the surface of the electrode, time studies were made of the stability of the AgCl surface. Gauzes containing ten mg of silver as AgCl were prepared, stored in eight M HNO₃ for varying periods of time and then used for a silver separation. The yields of the exchange determined under quantitative conditions are shown in Table VII. The period of study extended over one week.

Table VII

Effect of Aging of the AgCl
upon the Efficiency of the Silver Exchange

Time of Aging in 8 M HNO ₃	Yield in 15 Minute Contact
2 hrs	99.0
22 hrs	99.8
72 hrs	99.5
7 days	98.7

No attempt was made to keep the gauzes from direct light. However, the only light incident upon the gauzes during this period was that from two 100-watt fluorescent tubes about four feet above them. It appears that the aging of AgCl gauzes in eight M HNO₃ for periods up to seven days has no effect on their activity with respect to the exchange separation of silver.

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