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The Removal of Iron and Manganese
From Gold by Chlorine Annealing

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# THE REMOVAL OF IRON AND MANGANESE FROM GOLD BY CHLORINE ANNEALING

By

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ABSTRACT

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FROM GOLD BY CHLORINE ANNEALING

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Gold of a much higher purity than is available commercially is required for the study of superconductivity in Au and the study of dilute gold rare earth alloys. The chlorine annealing process is known to remove relatively high concentrations of iron from gold. This work describes the use of the radionuclides Fe–59 and Mn–54 to study the effectiveness of this process in removing very low levels of these impurities from gold. This process is found to be very effective in removing Mn–54 from Au, even with very low chlorine pressures (< 0.1 microns). Iron is also removed to very low levels although there seem to be inhibiting mechanisms of unknown origin at work in this case. Finally, the method is ineffectual in removing iron oxides.

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# I. INTRODUCTION

Considerable interest currently exists in the obtainment of high purity gold, since researchers are actively conducting experiments which require the use of gold of a much higher purity than is available commercially (impurity levels at about 1 ppm). The need for high purity gold is exemplified by the following. (1) The investigation of an intrinsic property, superconductivity. Gold is predicted to become superconducting at approximately 0.2 mK. Recently gold was studied to $4.2 \times 10^{-5}$ K,[1] and no superconductivity was observed. This lack of superconductivity was attributed to the presence of magnetic impurities in the gold, particularly iron (which was present at about the 0.5 ppm level). (2) The study of dilute magnetic alloys which contain known magnetic impurities. Magnetic impurities in non-magnetic hosts have been studied for over 30 years. One interesting behavior is now known as the "Kondo Effect": below approximately 4 K temperatures, the resistance of a sample rises as the temperature is lowered due to the scattering of conduction electrons off of the magnetic impurities.[2] Gold samples containing small amounts of magnetic rare earth impurities are being studied in this laboratory. For the Au(Yb) system it has been observed here and in France that 1 ppm levels of iron in the gold can affect the resistivity of the sample to the same degree as 400 ppm of Yb.[3] Thus, there is a need to develop techniques which reduce the levels of magnetic impurities, in particular iron, in the gold.

During 1969 C.W.E. Walker developed a method for removing iron impurities from gold wires.[4] His "chlorine gas anneal" procedure consists of the

following steps: (1) insert the gold wire into a quartz tube and evacuate it, (2) admit 1,000 microns of hydrogen gas and then heat at 850°C for 0.5 hour, (3) remove the hydrogen and replace it with 100 to 300 microns of chlorine gas, and (4) after the desired time, remove the chlorine and then allow the gold to return to room temperature.

It is thought that the iron removal occurs in the following manner: any iron oxide present in the gold is first reduced by the hydrogen gas. Free iron atoms which diffuse to the surface of the gold immediately react with the chlorine gas to form volatile chloride compounds which then evaporate away ($FeCl_3$ boils at 315°C while $FeCl_2$ sublimes above this temperature).

Although $FeCl_2$ and $FeCl_3$ are volatile at much lower temperatures, 850°C was chosen to ensure that the rate of diffusion of the iron would be as fast as possible, but that the amount of gold lost through vaporization would be minimal. Also, the formation of any gold chloride compounds must be prevented. The chosen temperature accomplishes this as AuCl decomposes at 170°C to $AuCl_3$ which in turn decomposes at 254°C.

By chlorine annealing for three days, Walker was able to reduce the iron content of a gold wire (0.1 mm in diameter) from an initial level of 2 ppm to 0.07 ppm. Carrier-distillation spectrographic analysis was used to determine the amount of iron present (the lower limit for detection by this procedure is about 0.07 ppm).

J. Kopp[5] has used Walker's procedure to purify gold and has subsequently observed changes in the resistivity and thermopower that are consistant with the removal of the iron from the gold. It should be noted, however, that these measurements are incapable of differentiating "passification" of the iron inside the gold from actual removal of the iron from the gold.

Here at MSU, chlorine annealing of gold has been done and results similar to those of Kopp have been observed. However, it was found that if the chlorine anneal was followed by a hydrogen anneal, the Kondo effect returned.[6] This indicates that some magnetic impurities are "passified" by the chlorine annealing (perhaps by formation of chlorine compounds), but are not removed.

Thus we want to study, with very low levels of magnetic impurities (below 0.07 ppm), the chlorine annealing process by a method that will enable the motion of the impurities to be observed. The use of a radioactive tracer will enable us to achieve this. The obvious tracer is $^{59}Fe$, a radionuclide that has a reasonably long half life (45 days). Upon decaying it emits 2 $\gamma$ rays (1.1 MeV and 1.3 MeV) which can easily be detected down to very low concentrations. We also wanted to see if the method would remove another magnetic impurity. We chose $^{54}Mn$ as this has a long half life (303 days), and it could be easily detected as it emits a 0.8 MeV $\gamma$ ray.

Pure gold pellets were rolled into thin gold foils (about 3 mm by 6 mm and about 0.1 mm thick). Iron-59 and manganese-54 were diffused into separate sets of foils: the initial level of impurity present was about $10^{-6}$ ppm. The foils were placed in a quartz tube, heated and annealed in chlorine gas during which a sodium iodide detector and a multichannel analyzer were used to follow the level of tracer present in the foils.

## II. APPARATUS AND EXPERIMENTAL PROCEDURE

### A. APPARATUS

The chlorine annealing apparatus, shown in Figure 1, consists of a pumping station (mechanical and diffusion pumps), a Pyrex "manifold" which interconnects five high-vacuum valves, a bottle with a high-vacuum valve to contain the chlorine, one Veeco thermocouple, a quartz tube, and an oven. Both the chlorine bottle and quartz tube have a ground-glass socket which fits over an o-ring ball joint on the manifold and is held in place by a Thomas clamp. The vacuum valves on the manifold allow the introduction and removal of gasses necessary for the experiment while preventing unwanted exposure of the foil to air during the annealing process. The thermocouple is attached to the manifold by a 3/8" quick connect (rubber o-ring type), and the manifold attaches to the pumping system via two quick connects in series (one 3/8" and one 5/8"; both are rubber o-ring types). The valves, ball joints, and sockets were covered with a thin layer of halogen-resistant vacuum grease.

Figure 2 shows the equipment used for detecting the radioactive iron and manganese. The system consists of an Eberline Mini-Scaler, which powers a 2" by 2" sodium iodide detector, and a Tracor Northern Multichannel Analyzer. The Tracor Northern analyzes the voltage pulses generated by the photomultiplier tube of the sodium iodide detector in response to incoming radiation.

Figures 3a and 3b show the geometries used during counting. Counts on the foils before and after completion of the chlorine annealing were done in a lead container to shield from background radiation: the sodium iodide detector and foil were positioned inside by a nylon holder. This is shown in Figure 3b. To determine the impurity level as a function of annealing time, counts were taken at regular intervals with the arrangement shown in Figure 3a. The oven was

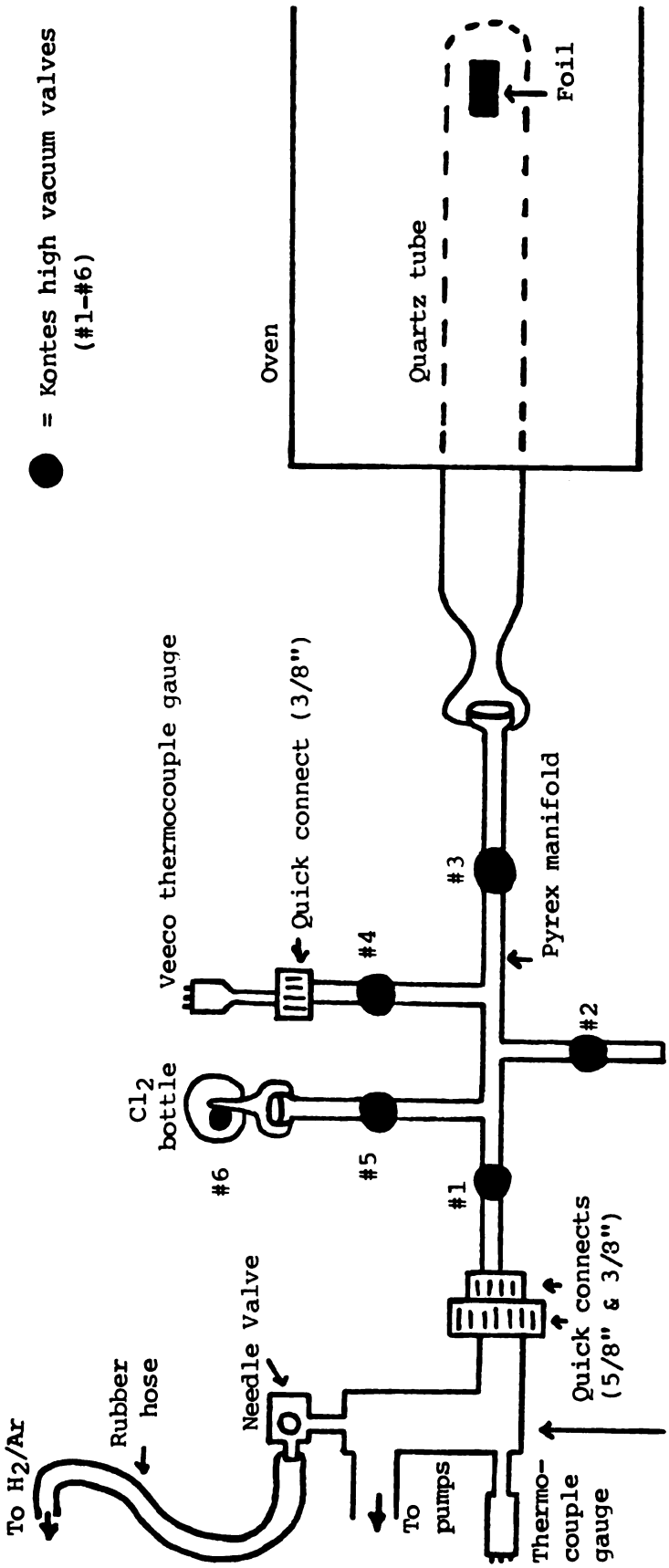


Figure 1. Chlorine Gas Annealing Apparatus (top view)

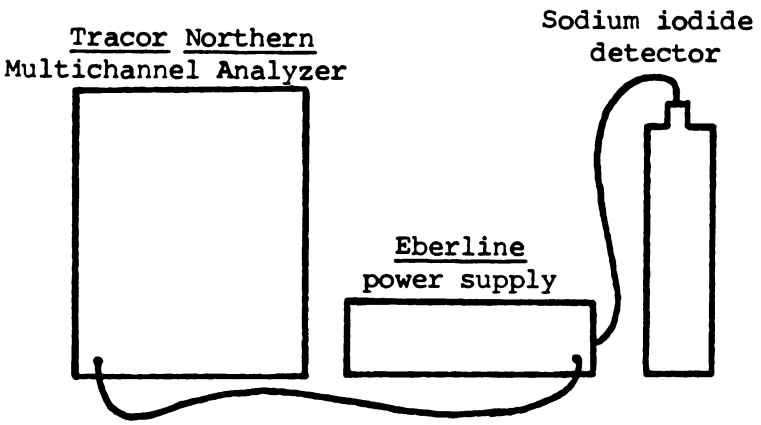


Figure 2. Counting Apparatus (side view)

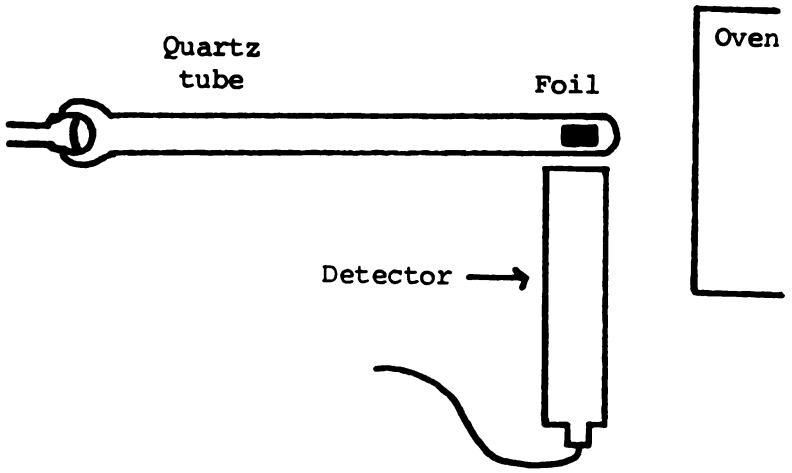


Figure 3a. Counting Arrangement 1 (top view)

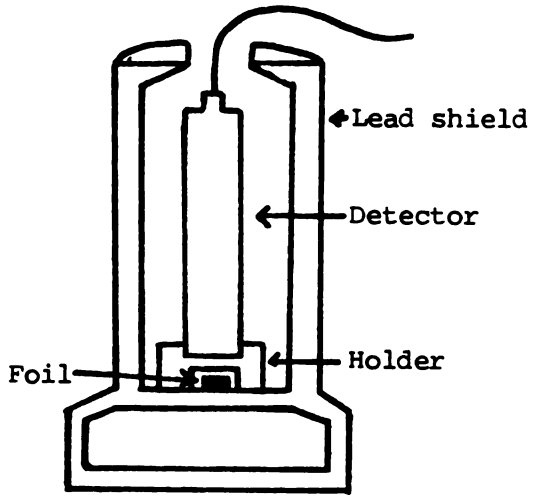


Figure 3b. Counting Arrangement 2 (side view)

pulled back from around the quartz tube, and the detector was positioned outside the tube near the foil for counting (it was not possible to make these counts in the lead container—once the anneal was started, the foil could not be exposed to air). After the count was completed, the oven was repositioned over the quartz tube.

B. PROCEDURE

1. Diffusion of the radioactive iron (or manganese) into the gold.

Before these nuclides could be removed by chlorine annealing they had to first be put into the gold. The radionuclides were purchased from New England Nuclear Corporation. The iron-59 came as ferric chloride in 0.5 M hydrochloric acid and the manganese-54 came as manganese dichloride, also in 0.5 M hydrochloric acid. The volume shipped of each was 0.1 ml, and the activity at the time of assay was $10^{-4}$ Curies. Both had radionuclide and chemical purities of 99% at the time of assay. The gold foils were rolled from gold pellets of 99.999% purity obtained from the Cominco America Company.

1. The gold foils (all about 3 mm by 6 mm and about 0.1 mm thick) were etched for several minutes in aqua regia (diluted 1:1 with distilled water) and rinsed multiple times, first in distilled water and finally in acetone.

2. A small amount of $FeCl_3$ (or $MnCl_2$) was mixed with a photographic wetting agent. This solution was applied to the foils with a small paintbrush. The use of a wetting agent resulted in an even distribution of the solution over the gold. (Note: the activity of fresh nuclide solution is about $3.7 \times 10^7$ disintegrations/sec. per ml of solution which, for iron, corresponds to $4.4 \times 10^9$ counts/min. per ml of solution. Thus, to make a foil with a one minute count of 20,000, $4.5 \times 10^{-6}$ ml of solution are required.)

3. The foils were allowed to dry overnight in air.

4. The foils were sealed in a length of quartz tubing (precleaned with aqua regia and out-gassed with a hand torch) under 1/4 atmosphere of a 10% hydrogen-90% argon mixture.

5. The foils were then heated for 3-5 days at 850°C to diffuse the iron (or manganese) into the gold.

6. After heating, one representative foil was progressively etched with aqua regia while counts were taken on the foil to be certain that the iron (or manganese) was uniformly diffused throughout the foil.

7. The remaining foils were given a 1.5 minute etch in dilute aqua regia (diluted 1:1 with distilled water) to remove any surface deposits of iron (or manganese) that might exist (this step was omitted on some foils).

8. The foils were stored in a dessicator under the hydrogen-argon mixture until used.

2. Eberline and Tracor Northern settings.

The Eberline Mini-Scaler was used to power the sodium iodide detector: its high voltage selector was set at 4.8. All voltage pulses created when radiation entered the detector went to the Tracor Northern Multichannel Analyzer. However, only those falling within a predetermined energy range were actually counted. The following settings were used on the Tracor Northern so that it would only count signals coming from the detector that had energies close to those of the $\gamma$'s emitted by the iron (or manganese).

| Dial on Tracor Northern | Iron | Manganese |
|---|---|---|
| Gain | 6.0 | 6.0 |
| Lower level discriminator | 5.0 | 3.5 |
| Upper level discriminator | 9.0 | 9.0 |
| Offset | 1024 | 768 |
| Conversion gain | 2048 | 2048 |
| Horizontal | full | 1/2 |
| Range | 150-800 | 162-442 |

3. Chlorine annealing the foils.

We believe that the Fe and Mn impurities in the foils were reduced to their atomic states since these elements were diffused into the gold in the presence of $H_2$. As a precaution most of these foils were stored in a dessicator under a

hydrogen-argon mixture to retard oxidation of these impurities. However, several of these foils were purposely oxidized. This was accomplished by inserting the foils in a quartz tube open to the atmosphere and heating at 850°C for 4.5 days.[7]

The following procedure was followed when chlorine annealing the foils (the admission of hydrogen was omitted for the low pressure anneals and for the anneals of the oxidized foils). The count rate of each foil was first measured in the lead container (see Figure 3b). Then the foil was placed inside the quartz tube of the annealing apparatus, and the system was pumped out to about $10^{-4}$ Torr. The chlorine was frozen into the bottle by surrounding the bottle with liquid nitrogen. The quartz tube was then filled with hydrogen, and the count rate of the foil, while in the tube, was measured (see Figure 3a). Next, the oven was slid over the quartz tube, and the foil was heated under hydrogen for a set time (this varied from essentially zero time to about one hour). The hydrogen was then pumped out with the diffusion pump, after which the chlorine was admitted by removing the liquid nitrogen and allowing the bottle to warm slightly. After the foil had annealed in the chlorine for the desired time, the chlorine was removed from the quartz tube by freezing it back into the bottle with the liquid nitrogen. Next, hydrogen was admitted to the foil to stop further formation of iron (or manganese) chloride compounds from any residual chlorine gas that might be present. The oven was pulled from around the tube, and the count rate of the foil was measured, after which the oven was replaced. This was repeated several times to ascertain the rate of removal of the iron (or manganese) by the method. As the anneal progressed, radionuclide compounds condensed on the inner surface of the tube at the cooler end of the tube, causing a considerable "background" which could not be separated from the count rate of the foil itself. Because of this, a "clean-tube" count was done at the end of each

run: the foil was placed in a clean quartz tube, maintaining the same experimental geometry, and the count rate was measured. A final count was taken with the foil placed in the lead container.

## III. PRESENTATION OF RESULTS AND DISCUSSION

The rate of removal of impurities by chlorine annealing is determined by how rapidly these impurities diffuse to the surface of the gold. Because the annealing process is diffusion limited, the mathematics of diffusion will be presented first so that the loss rate of the impurities from the foils can be analyzed in terms of a diffusion coefficient.[8] Then the experimental results will be summarized and discussed. Detailed tabulations of the data are in the Appendices.

Since the thickness of each foil is much less than its other two dimensions, the diffusion process is essentially one-dimensional. In one dimension the diffusion equation is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right) . \tag{1}$$

Here, c is the concentration of impurity present, and D is the diffusion coefficient. For homogeneous cubic crystals, D is isotropic and independent of position so the equation becomes

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} . \tag{2}$$

This equation can be solved by the separation of variables technique. A solution of the form

$$c(x,t) = X(x)\, T(t) \tag{3}$$

is assumed and substituted into Eq. (2). This leads to the following Fourier-series solution

$$c(x,t) = \sum_{n=1}^{\infty} (A_n \sin \lambda_n x + B_n \cos \lambda_n x) \exp(-\lambda_n^2 Dt). \qquad (4)$$

This equation is a general equation which must be made to fit the assumed boundary conditions. The boundary conditions for a foil of thickness h with boundaries at x = 0 and x = h are

$$c = c_o \text{ for } 0 < x < h, \text{ at } t = 0$$

$$c = 0 \text{ for } x = h \text{ and } x = 0, \text{ at } t > 0.$$

We will justify later the above assumption that the initial concentration of impurities is uniform throughout the foil. The solution becomes

$$c(x,t) = \frac{4c_o}{\pi} \sum_{j=0}^{\infty} \left(\frac{1}{2j+1}\right) \sin\left[\frac{(2j+1)\pi x}{h}\right] \exp\left[-\left(\frac{(2j+1)\pi}{h}\right)^2 Dt\right]. \qquad (5)$$

However, it is not possible, in this experiment, to determine concentration of the impurity at various depths in the gold, so the average concentration $\bar{c}$ is required:

$$\bar{c} = \frac{1}{h} \int_0^h c(x,t)dx = \frac{8c_o}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp\left[-\left(\frac{(2j+1)\pi}{h}\right)^2 Dt\right]. \qquad (6)$$

Each successive term in Eq. (6) is smaller than the preceding one. For $\bar{c}/c_o \leq 0.8$, the first term is an excellent approximation to the solution. This approximate solution is

$$\bar{c} = \frac{c_o 8}{\pi^2} \exp\left(\frac{-\pi^2 Dt}{h^2}\right). \qquad (7)$$

Thus, once $\bar{c} \leq 0.8\ c_o$, most of the impurities near the surface have left the foil, leaving behind an impurity distribution of the form

$$c = c_o \sin\left(\frac{\pi x}{h}\right). \qquad (8)$$

Thus, Eq. (7) can be used to calculate D from the slope of the data on a semi-log plot of counts/min. versus time. The equation for D is, then,

$$D = \frac{(\text{slope})h^2}{2} . \qquad (9)$$

First, the uniformity of the impurity distribution in the foils will be discussed. This will be followed by a discussion of the experimental results of chlorine annealing Au($^{54}$Mn) foils and ended by a similar discussion for Au($^{59}$Fe) foils.

## A. IMPURITY DISTRIBUTION IN FOILS

To check the assumption that initially the radionuclides were uniformly distributed throughout the foils, two foils were progressively etched in aqua regia while counts were taken on the foils. Figure 4 is a graph showing the relationship between remaining count rate and foil mass for both an Au($^{54}$Mn) foil and an Au($^{59}$Fe) foil. These points fall very close to the theoretical straight line drawn on the graph. Thus, the initial concentration of impurities is close to uniform throughout the foils.

## B. RESULTS FOR CHLORINE ANNEALING OF Au($^{54}$Mn) FOILS

Table 1 is a summary of the important experimental results. Figure 5 shows the normalized count rate as a function of annealing time for Run 20 where the foil was annealed in a chlorine pressure of 100 microns. These data are typical of the Au($^{54}$Mn) foils studied so far. Except for very short and very long annealing times, the data fall on a straight line. To determine the slope of the data over the intermediate times, a weighted least-squares computer fitting

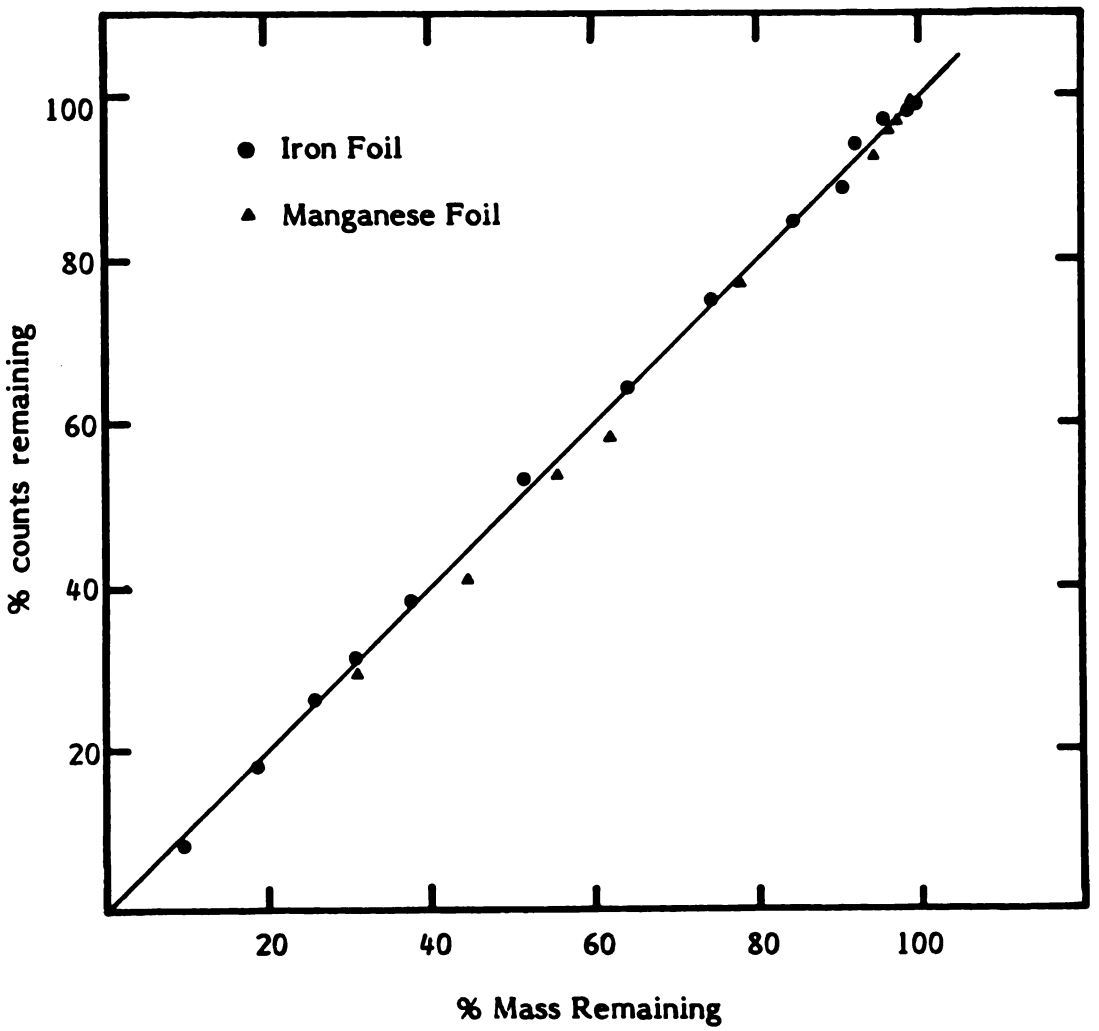


Figure 4. Etch Tests of Gold Foils

Table 1. Summary of Chlorine Anneals of Au($^{54}$Mn) Foils

| Run | Temp. (°C) | Pressure $Cl_2$ (microns) | Initial shielded count rate ($min^{-1}$) | Final shielded count rate ($min^{-1}$) | Time in $Cl_2$ (hours) | Thickness of foil (cm) ±0.0001 | Slope ($hours^{-1}$) | D ( x $10^{-10}cm^2/sec$) |
|---|---|---|---|---|---|---|---|---|
| 11* | 770 | <0.1 | 17,929±67 | 297±13 | 46.4 | 0.0117 | 0.109 ± 0.002 | 4.2 ± 0.1 |
| 17* | 770 | <0.1 | 9,079±48 | 14±6 | 68.1 | 0.0094 | 0.181 ± 0.006 | 4.5 ± 0.2 |
| 20** | 770 | 100 | 10,664±53 | 201±9 | 30.2 | 0.0122 | 0.124 ± 0.001 | 5.2 ± 0.1 |
| 19** | 770 | 1,000 | 11,312±62 | 147±10 | 49.1 | 0.0118 | 0.164 ± 0.002 | 6.4 ± 0.1 |
| 22** | 850 | 100 | 11,517±62 | 17±4 | 12.6 | 0.0104 | 0.529 ± 0.012 | 16.1 ± 0.5 |
| 33*** | 850 | 100 | 12,906±57 | 55±6 | 6.0 | 0.0086 | 0.885 ± 0.010 | 18.4 ± 0.5 |

*No hydrogen introduced at all.

**Foil heated in hydrogen for roughly 5 minutes before admission of chlorine.

***Foil heated in hydrogen for about 1 hour before admission of chlorine.

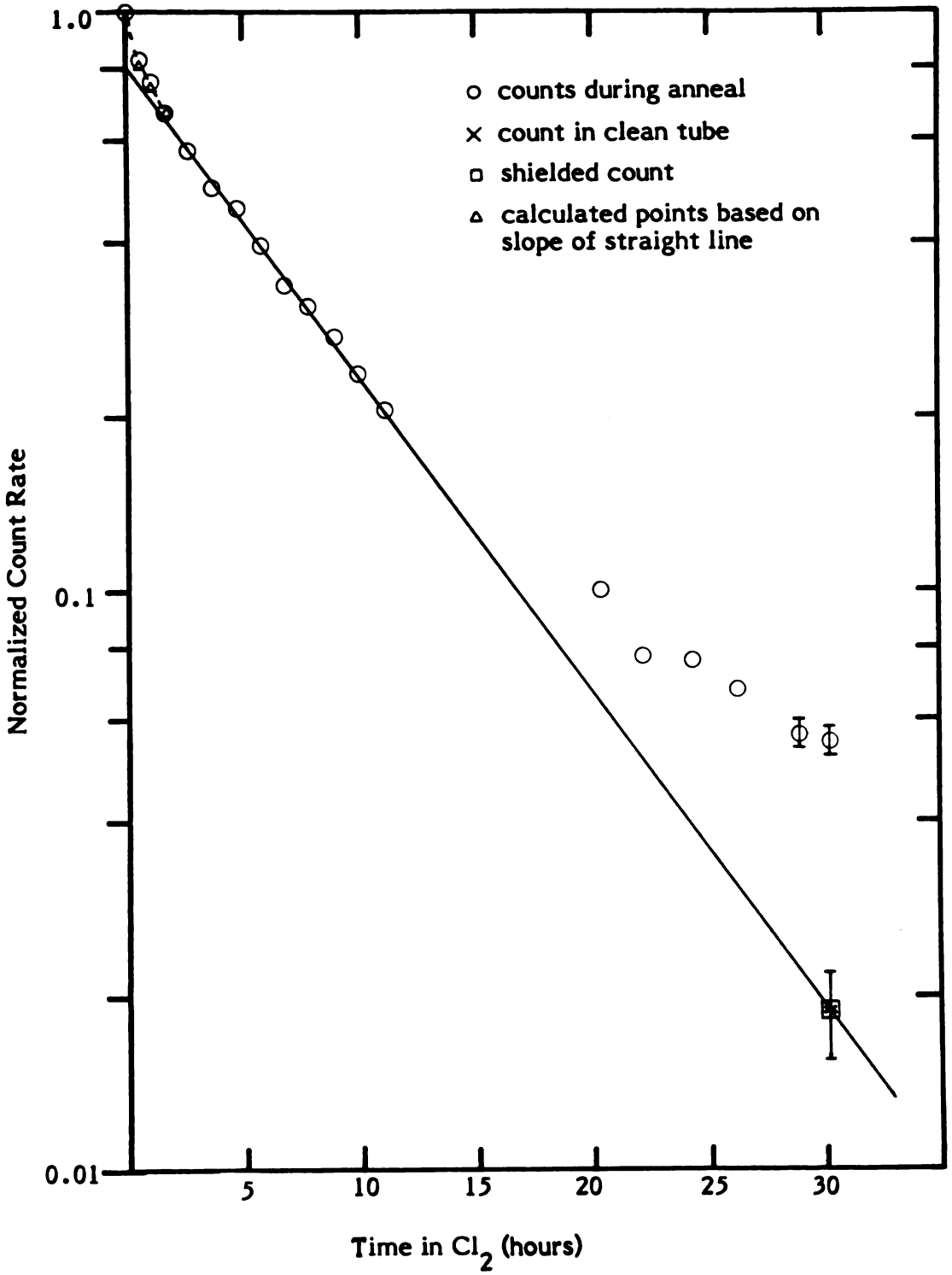


Figure 5. Run 20

procedure was employed. This straight-line fit extrapolates to a zero-time normalized count rate of 0.813 $\pm$ 0.007 which is in excellent agreement with the t = 0 limit of Eq. (7) with

$$\frac{\bar{C}}{C_o} = \frac{8}{\pi^2} = 0.811 \, . \qquad (10)$$

The dotted curve in Figure 5 was obtained from Eq. (6) using the slope calculated from Eq. (7). The agreement of this curve with the data is excellent. With the exception of Run 17, all of the Au($^{54}$Mn) foils exhibit this more rapid loss of count rate at short times.

Counts taken for large times (t > 15 hours) also fail to follow a simple exponential decay. As discussed in the Procedure Section, this is due to the accumulation of $^{54}$Mn on the inner surface of the quartz tube as the annealing progresses. Because it was not possible to effectively shield the detector from this "background" radiation, $\gamma$ rays emitted by this condensate were detected as well as those arising from the foil itself. At the end of the Run the foil was put into a clean quartz tube, while maintaining the same experimental geometry, and a count was taken. It is seen in Figure 5 that this "clean tube" count rate falls nicely on the extrapolation of the straight-line behavior. The datum point for the final shielded count rate (normalized) is also plotted in Figure 5, and it agrees well with the clean-tube count rate. All of the determinations of the slopes in Table 1 include these clean-tube and shielded counter points in the slope computation (for all experiments the data points actually used in slope determination are indicated in Appendix B).

If long-time count rates are falsely high due to the "background" radiation, perhaps the intermediate-time count rates are affected to some extent as well. However, for these intermediate points the extrapolated t = 0 count rate agrees with the t = 0 prediction of Eq. (7), and the t = 30 hour extrapolation agrees with

the clean tube count rate. Hence, it would appear that these background effects are minimal (barring some bizarre contributions that sum to give a false exponential decrease in this region).

During Run 11, one set of count rates on the tube itself as a function of distance from the foil was taken at 21 hours. The count rate appeared to be uniform along the portion of the tube that was located in the hotter portion of the oven and was a maximum where the heating elements of the oven ended (approximately 14 cm from the foil, where the oven is about 200°C cooler than the central portion of the oven). The count rate was still quite high at the oven exit (approximately 8 cm beyond the end of the heating elements). The distribution of radionuclides along the tube may continually change during the anneal since the tube is subjected to repeated heating and cooling while measurements are taken. The introduction of hydrogen may also alter the distribution. If this redistribution occurs, the contribution of this background to the foil count rate will be difficult to predict.

This background radiation could be reduced by using a longer oven (hotter over a wider region) and a longer quartz tube. In this way, the condensate would be located farther from the gold foil.

Figure 6 is a graph of the Run 11 data where the foil was annealed at low chlorine pressure (approximately 0.1 micron). This plot shows all of the features present in Figure 5 (such as the rapid decrease in the count rate for short annealing times and the good extrapolation to the clean-tube count rate at 21 hours). These data were graphed to illustrate the effects of filling the annealing apparatus with air before the completion of the chlorine anneal. In order to measure the contribution of the background radiation, a clean-tube count rate was taken which required exposing the cool foil to the atmosphere. After this count, the foil was put back into the dirty tube and chlorine annealed further. At

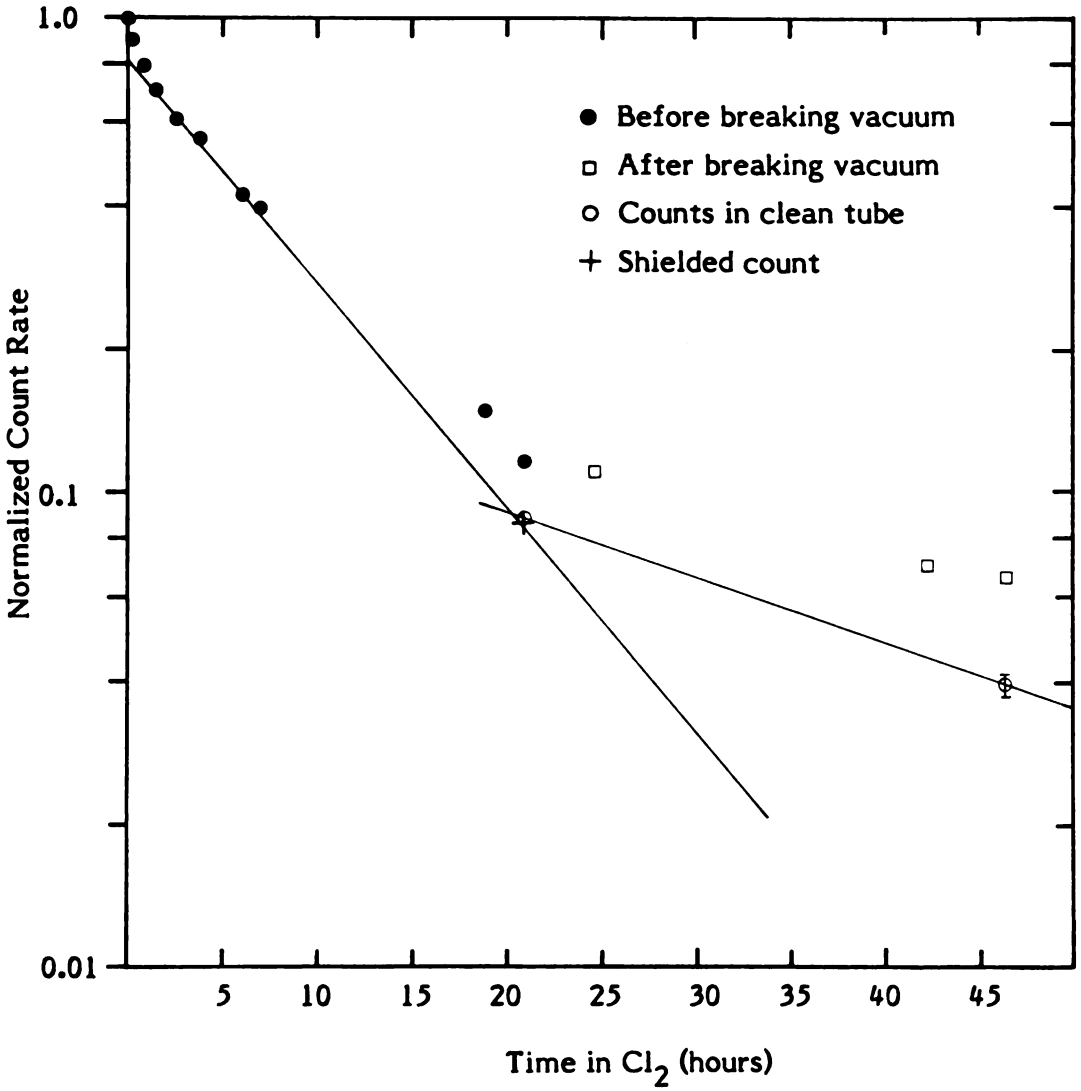


Figure 6. Run 11

the end of the experiment a count was taken in the clean tube as usual. The result of exposing the system to air was a decrease in the rate of manganese removal from the gold. This is shown in Figure 6; clearly there are two different rates present (compare with the single rate of Figure 5). The data of Run 17, tabulated in Appendix B, but not graphed, also exhibit a decrease in the rate of manganese removal upon venting the system before the anneal was finished. As a result, no subsequent experiments ($\geq$ Run 20) had foils exposed to the air until the anneal was completed.

Run 19 was an anneal done in 1,000 microns of chlorine. This high pressure anneal was done in order to investigate the possibility that some of the chlorine would diffuse into the gold and form Mn-chloride compounds inside the gold. These compounds might remain inside the gold rather than boiling away (Mn-chloride compounds, being rather large, might not diffuse readily through gold). To the contrary, the values of D in Table 1 seem to indicate that $^{54}$Mn atoms come out more rapidly at higher chlorine pressures, which argues against the formation of Mn-chlorides inside the gold.

Runs 22 and 23 were performed to answer two questions: (1) how does D change as the temperature is raised, and (2) will preheating the foil in hydrogen for an extended period alter the rate of removal of the manganese? The motivation behind this latter question is as follows: after the $^{54}$Mn atoms are diffused into the foils, the foils are stored under hydrogen to retard oxidation of the manganese; however, some of these foils were stored for as long as a month before they were chlorine-annealed, so some oxidation may have occurred. It was thought that preheating in hydrogen might reverse any oxidation that might have taken place. Clearly, raising the temperature caused a substantial increase in the diffusion coefficient (see Table 1). Table 1 also shows that the preheating in hydrogen caused a slight increase in D. Finally, it should be noted that these

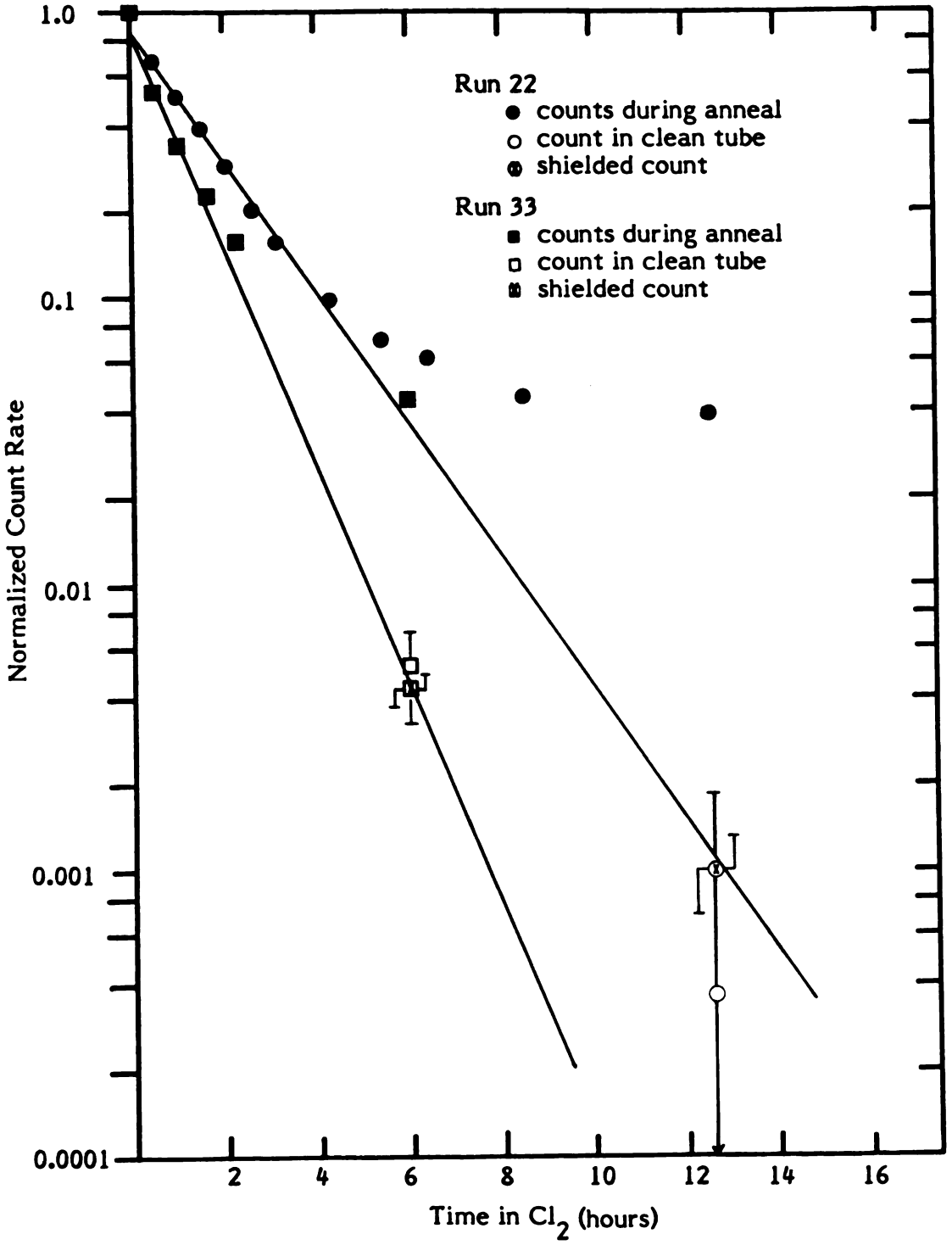


Figure 7. Runs 22 and 33

two experiments also show the non-exponential behavior at very short and very long annealing times, which we have seen for other samples (see Figure 7).

## C. RESULTS FOR CHLORINE ANNEALING OF Au($^{59}$Fe) FOILS

The important experimental results are listed in Table 2. Those experiments illustrating major features of the chlorine-annealing process for Au($^{59}$Fe) are graphed in Figure 8.

It was found that the rate of impurity removal during the chlorine annealing of Au($^{59}$Fe) foils did not follow the simple time dependence that was obtained with Au($^{54}$Mn) foils. Also, the results were not as reproducible. This can be seen from Runs 23 and 26. The extrapolations of the intermediate-time points (time = 1-5 hours) fail to include the clean-tube and shielded count rates. Indeed the count rate of Run 26 seems to be leveling off, suggesting that some fraction of the $^{59}$Fe was going to remain in the foil permanently.

Run 24 used a foil that had been prepared as outlined in the procedure, but was then heated in air for three days to oxidize the $^{59}$Fe inside the gold foil. As seen in Figure 8, little of the iron was removed from the foil during the chlorine anneal. Thus, chlorine annealing does not remove iron oxide compounds to any appreciable extent.

Since it is clear that oxygen can inhibit the effectiveness of chlorine annealing, there arose the possibility that the somewhat unpredictable behavior of the data was due to the presence of varying amounts of iron oxides in the foils used (even though the foils had been stored under hydrogen). Run 32 was performed to test this idea. The foil was preheated at 850$^{o}$C in hydrogen for one hour prior to exposure to chlorine. This resulted in a better exponential decay which seemed to extrapolate to the clean-tube and shielded points. However,

Table 2. Summary of Chlorine Anneals for Au($^{59}$Fe) Foils

| Run | Temp. (°C) | Pressure $Cl_2$ (microns) | Initial shielded count rate ($min^{-1}$) | Final shielded count rate ($min^{-1}$) | Time in $Cl_2$ (hours) | Thickness of foil (cm) ±0.0001 | Slope ($hours^{-1}$) | D ( x $10^{-10}cm^2/sec$) |
|---|---|---|---|---|---|---|---|---|
| 30+ | 850 | <0.1 | 11,498±55 | 2,713±31 | 10.4 | 0.0102 | 0.126 | 3.7 |
| 23++ | 850 | 100 | 4,795±38 | 110±10 | 13.3 | 0.0097 | 0.311 ± 0.019 | 8.2 ± 0.5 |
| 26++ | 850 | 100 | 11,698±55 | 1,052±24 | 12.7 | 0.0089 | 0.251 ± 0.024 | 5.6 ± 0.5 |
| 28++x | 850 | 100 | 33,277±91 | 90±9 | 25.4 | 0.0091 | 0.246 | 5.7 |
| 24* | 850 | 100 | 4,734±35 | 3,791±31 | 14.8 | - | - | - |
| 32** | 850 | 100 | 14,422±61 | 216±9 | 6.9 | 0.0069 | 0.559 ± 0.014 | 7.5 ± 0.3 |

+No hydrogen introduced at all.

++Foil preheated in hydrogen for about 5 minutes before the admission of hydrogen.

xContinuous, uninterrupted chlorine anneal.

*Foil thoroughly oxidized: no hydrogen admitted at all.

**Foil preheated at 850°C in hydrogen for about 1 hour before the admission of hydrogen.

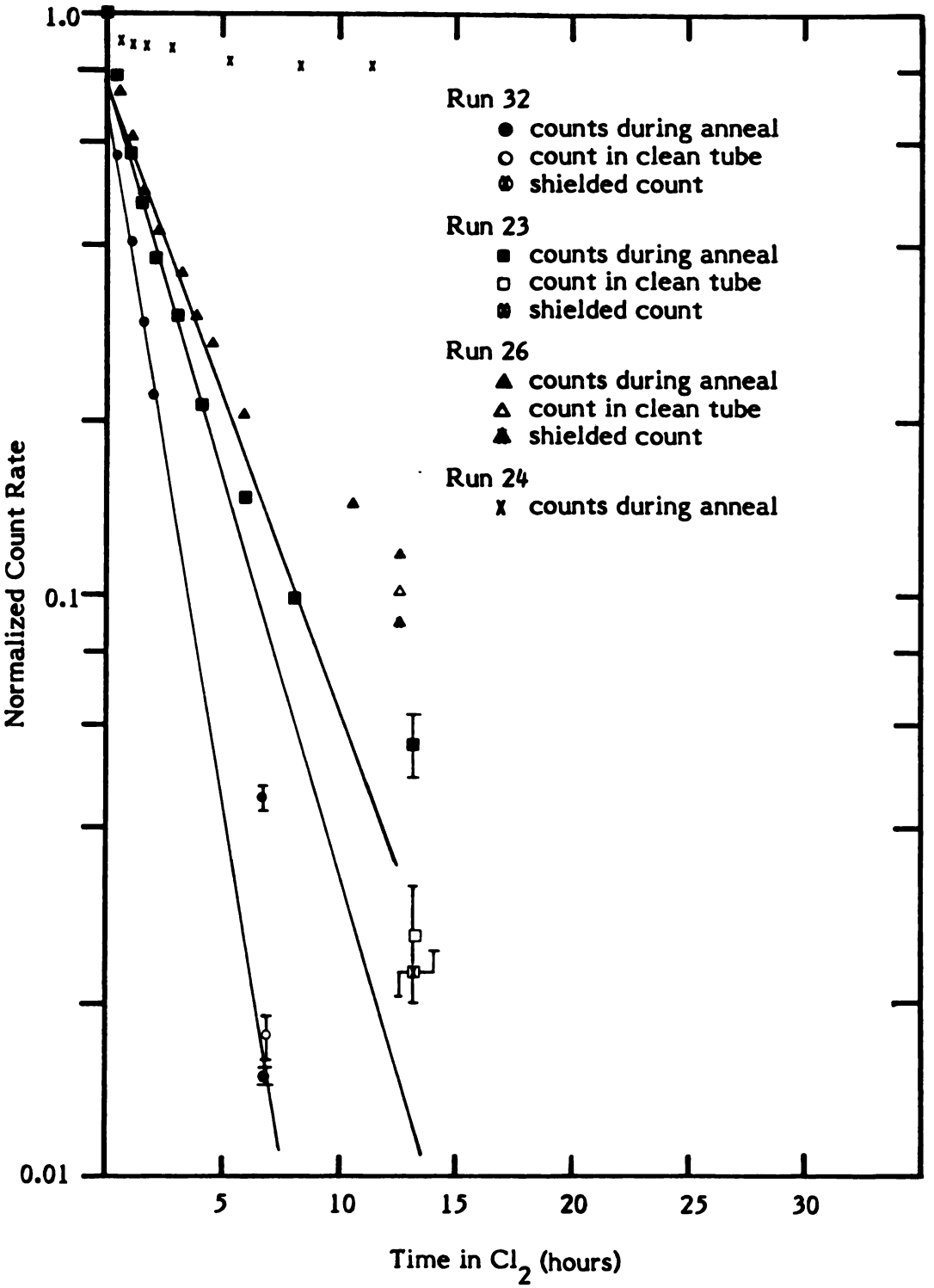


**Figure 8. Runs 32, 23, 26, and 24**

after the 13 hours of chlorine annealing, the Run 26 foil was also heated at 850°C in hydrogen for 14 hours (after the shielded count had been taken), and then chlorine annealed for 2 hours. The count rate dropped by only 25% in these 2 hours in comparison with an expected 60% reduction. Thus, this length of hydrogen anneal appears not to restore the loss rate during chlorine annealing to the value originally observed in this foil. This result would seem to contradict Run 32. In addition, it should be pointed out that Run 28 (listed in Table 2, but not graphed) was performed with a foil treated just like Runs 23 and 26, except that this anneal was an uninterrupted 24.5-hour chlorine anneal. At the end of this anneal the normalized count rate had dropped to the very low value of 0.0026. We conclude that chlorine annealing can remove iron to very low levels, but that there are unknown mechanisms at work which can inhibit the removal of the iron. At this time, we do not know if these mechanisms are associated with the initial state of the foils prior to the chlorine anneals or with our annealing procedures.

Diffusion coefficients were difficult to obtain because of the non-exponential decays. However, the data between 1 and 5 hours were arbitrarily chosen to define the slopes in order to obtain D values (except for Run 32 where the clean-tube and shielded count rates were used). The lines drawn on Figure 8 represent fits to these arbitrary points.

Runs 23, 26, 28, and 32 were all done at a chlorine pressure of 100 microns, and all gave similar D's. These values of D compare reasonably well with Walker's result of $(5.7 \pm 0.9) \times 10^{-10}$ cm$^2$/sec for iron in gold.[4] Note that the foil for Run 30 was annealed in low pressure chlorine and has a smaller D, as was the case for Au($^{54}$Mn).

Although a 1,000-micron pressure chlorine anneal has not, as yet, been done, the tabulated diffusion coefficients indicate that the higher chlorine

pressures do not cause a decrease in the intermediate-time diffusion rate which might occur if iron chloride compounds formed inside the foils.

## IV. CONCLUSIONS

Our radioactive tracer technique has shown that chlorine annealing effectively removes very low levels of manganese from gold, even when the chlorine pressure is below $10^{-4}$ Torr. Manganese impurity levels, initially about $10^{-6}$ ppm, were reduced by a factor of 100 in 5 to 9 hours by annealing in 100 microns of chlorine gas at 850°C. To our knowledge, this work represents the first measurement of D for manganese in gold.

The result of a 1,000-micron chlorine anneal indicates that high pressures of chlorine simply result in faster removal of the Mn: there is no evidence to suggest intragold formation of manganese chloride compounds resulting from the diffusion of the chlorine into the gold.

The Au(Mn) system exhibits the Kondo effect, and its resistance is expected to continue rising as the temperature is lowered even below $10^{-3}$K. In order that the magnetic interaction between the Mn atoms not interfere with the Kondo effect, very dilute alloys would be required for studies near $10^{-3}$K. The success in removing manganese suggests that the chlorine annealing process might be an effective means of producing extremely dilute Au(Mn) alloys from better characterized more concentrated Au(Mn) alloys.

Low levels of iron impurities were also removed by the annealing procedure. However, the results indicate that there may be inhibiting mechanisms at work, and further work on this system is needed in order to better understand these mechanisms. Also, this work clearly shows that the chlorine annealing method is ineffectual in removing iron oxide compounds. Thus, gold

thought to contain these oxides must be thoroughly hydrogen-annealed prior to chlorine annealing.

Before proceeding with additional studies on the method, it would be worthwhile improving the counting geometry. As was mentioned in the discussion of Au($^{54}$Mn), a longer oven and a longer annealing tube would result in the radioactive condensate being located further from the gold, thus reducing the "background." Also, this would provide room to introduce lead shielding which would further reduce the detection of unwanted radiation. Finally, the use of a well counter would enable us to better focus counting on the foil itself.

We believe the method can be used to remove other impurities from gold, such as silver, copper, calcium, and chromium. For example, it would be straightforward to study the removal of Cr. The radionuclide $^{51}$Cr has a half-life of 28 days and emits a $\gamma$ ray at 320 KeV.

Finally, we have begun to investigate the possibility of using the method to remove iron from other metals, in particular, palladium. Our initial attempt to chlorine anneal Pd encountered difficulties; the Pd foil reacted with the chlorine and was lost. However, the annealing tube, which had contained the foil, showed one region of high count rate which was located at a region of the tube cooler than the region where it appeared that $PdCl_2$ had condensed. This indicates some separation of the iron from the palladium. The next anneal will be at much higher temperatures (1400$^{o}$C) so that a significant fraction of the Fe can diffuse to the surface in a time short enough to minimize the corrosion of the foil.

# V. BIBLIOGRAPHY

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# VI. APPENDICES

## APPENDIX A. Impurity Distribution in Foils

Table 1A. Foil Etch

| Iron | | Manganese | |
|---|---|---|---|
| % Mass Au left | % Count/ min left | % Mass Au left | % Count/ min left |
| 100.0 | 100.0 | 100.0 | 100.0 |
| 99.1 | 98.7±.9 | 99.7 | 99.5±.7 |
| 98.4 | 98.0 | 97.9 | 97.6 |
| 95.6 | 97.0 | 96.3 | 95.6 |
| 92.0 | 94.0 | 94.3 | 92.8 |
| 88.7 | 90.8 | 89.0 | 89.0±.7 |
| 84.6 | 84.7±.8 | 78.0 | 77.1 |
| 74.7 | 75.0 | 62.0 | 58.0 |
| 64.0 | 64.2 | 55.3 | 53.8 |
| 51.7 | 53.2 | 44.4 | 41.8 |
| 37.4 | 38.1 | 31.0 | 29.1±.4 |
| 30.8 | 31.1 | | |
| 25.7 | 26.1 | | |
| 18.4 | 18.0±.4 | | |

APPENDIX B. Chlorine Anneals of Au($^{54}$Mn) Foils

Table 1B. Run 11. Low Pressure $Cl_2$ Anneal of Au($^{54}$Mn) Foil (770°C)

| Count rate/min of foil while in tube | Total time in chlorine (hours) |
|---|---|
| 13,862 ± 85 | zero |
| 12,425 ± 100 | 0.3 |
| 10,976 ± 76 | 0.9 |
| 9,764 ± 72* | 1.5 |
| 8,469 ± 67* | 2.6 |
| 7,754 ± 64* | 3.9 |
| 5,877 ± 56* | 6.1 |
| 5,519 ± 55* | 7.0 |
| 2,048 ± 36 | 18.9 |
| 1,737 ± 33 | 20.9 |
| 1,119 ± 28*+ | 20.9 |
| 1,191 ± 22*++ | 20.9 |
| 1,583 ± 32 | 24.6 |
| 973 ± 27 | 42.2 |
| 917 ± 26 | 46.4 |
| 549 ± 23+++ | 46.4 |

Initial Shielded Count Rate/Minute = 17,929 ± 67
Final Shielded Count Rate/Minute = 297 ± 13
Thickness of Foil (centimeters) = 0.0117 ± 0.0001
Diffusion Coefficient ($cm^2$/sec) = $(4.2 \pm 0.1) \times 10^{-10}$

*Data used to determine diffusion coefficient.

+Anneal stopped, foil removed and counted in a clean tube after which foil was returned to original tube and anneal continued.

++This is a shielded count that has been corrected as follows: (1191 ± 22) = (13,862/17,929)(1,540 ± 28).

+++Foil counted in a clean tube at end of experiment.

## APPENDIX B. Chlorine Anneals of Au($^{54}$Mn) Foils

Table 2B. Run 17. Low Pressure $Cl_2$ Anneal of Au($^{54}$Mn) Foil (770°C)

| Count rate/min of foil while in tube | Total time in chlorine (hours) |
|---|---|
| 5,991 ± 57 | zero |
| 5,300 ± 54 | 0.6 |
| 4,695 ± 51* | 1.2 |
| 4,162 ± 48* | 1.7 |
| 3,311 ± 44* | 2.9 |
| 2,933 ± 41* | 3.9 |
| 2,407 ± 38* | 4.9 |
| 2,241 ± 37 | 5.9 |
| 1,749 ± 34 | 7.0 |
| 1,566 ± 32 | 8.0 |
| 1,389 ± 31 | 9.0 |
| 1,249 ± 30 | 10.0 |
| 920 ± 27*+ | 10.0 |
| 794 ± 25 | 11.1 |
| 370 ± 18 | 21.1 |
| 328 ± 18 | 22.7 |
| 306 ± 20 | 24.1 |
| 259 ± 20 | 26.2 |
| 222 ± 19 | 28.2 |
| 182 ± 19 | 32.3 |
| 117 ± 18 | 68.1 |

Initial Shielded Count Rate/Minute = 9,079 ± 48
Final Shielded Count Rate/Minute = 14 ± 6
Thickness of Foil (centimeters) = 0.0094 ± 0.0001
Diffusion Coefficient ($cm^2$/sec) = $(4.5 \pm 0.2) \times 10^{-10}$

*Data used to determine diffusion coefficient.

+Anneal stopped while dirty tube was replaced with a clean tube.

APPENDIX B. Chlorine Anneals of Au($^{54}$Mn) Foils

Table 3B. Run 20. 100 Micron $Cl_2$ Anneal of Au($^{54}$Mn) Foil (770°C)

| Count rate/min of foil while in tube | Total time in chlorine (hours) |
|---|---|
| 7,366 ± 63 | zero |
| 6,020 ± 57 | 0.6 |
| 5,547 ± 55 | 1.1 |
| 4,921 ± 52* | 1.7 |
| 4,271 ± 49* | 2.7 |
| 3,630 ± 45* | 3.8 |
| 3,333 ± 44* | 4.8 |
| 2,885 ± 41* | 5.8 |
| 2,552 ± 39* | 6.9 |
| 2,255 ± 37* | 7.9 |
| 2,013 ± 36* | 9.0 |
| 1,740 ± 34* | 10.0 |
| 1,508 ± 32* | 11.1 |
| 752 ± 25 | 20.4 |
| 571 ± 23 | 22.1 |
| 563 ± 23 | 24.3 |
| 496 ± 22 | 26.3 |
| 441 ± 22 | 28.9 |
| 407 ± 21 | 30.2 |
| 139 ± 18*+ | 30.2 |

Initial Shielded Count Rate/Minute = 10,664 ± 53

Final Shielded Count Rate/Minute = 201 ± 9 (139 ± 6*++)

Thickness of Foil (centimeters) = 0.0122 ± 0.0001

Diffusion Coefficient ($cm^2$/sec) = (5.2 ± 0.1) x $10^{-10}$

*Data was used to determine diffusion coefficient.

+Foil counted in a clean tube at end of experiment.

++This is a shielded count corrected as follows:
(139 ± 6) = (7,366/10,664)(201 ± 9).

APPENDIX B. Chlorine Anneals of Au($^{54}$Mn) Foils

Table 4B. Run 19. 1,000 Micron $Cl_2$ Anneal of Au($^{54}$Mn) Foil (770°C)

| Count rate/min of foil while in tube | Total time in chlorine (hours) |
|---|---|
| 7,633 ± 64 | zero |
| 6,292 ± 59 | 0.6 |
| 5,491 ± 55* | 1.1 |
| 4,917 ± 52* | 1.8 |
| 4,053 ± 48* | 2.9 |
| 3,375 ± 44* | 4.0 |
| 2,799 ± 41* | 5.1 |
| 2,576 ± 40 | 6.2 |
| 2,245 ± 38 | 7.3 |
| 1,896 ± 35 | 8.7 |
| 1,612 ± 33*+ | 8.7 |
| 512 ± 23 | 20.2 |
| 416 ± 22 | 22.2 |
| 373 ± 22 | 27.0 |
| 298 ± 21 | 29.8 |
| 237 ± 20 | 42.9 |
| 235 ± 20 | 46.0 |
| 224 ± 20 | 49.1 |
| 146 ± 19++ | 49.1 |

Initial Shielded Count Rate/Minute = 11,312 ± 62
Final Shielded Count Rate/Minute = 147 ± 10
Thickness of Foil (centimeters) = 0.0118 ± 0.0001
Diffusion Coefficient ($cm^2$/sec) = $(6.4 \pm 0.1) \times 10^{-10}$

*Data used to determine diffusion coefficient.

+Anneal stopped while dirty tube was replaced with a clean tube.

++Foil counted in a clean tube at end of experiment.

APPENDIX B. Chlorine Anneals of Au($^{54}$Mn) Foils

Table 5B. Run 22. 100 Micron $Cl_2$ Anneal of Au($^{54}$Mn) Foil (850°C)

| Count rate/min of foil while in tube | Total time in chlorine (hours) |
|---|---|
| 8,014 ± 66 | zero |
| 5,346 ± 55* | 0.5 |
| 4,029 ± 48* | 1.0 |
| 3,127 ± 43* | 1.6 |
| 2,328 ± 38* | 2.1 |
| 1,639 ± 33* | 2.7 |
| 1,244 ± 30* | 3.2 |
| 786 ± 26 | 4.3 |
| 570 ± 24 | 5.4 |
| 497 ± 23 | 6.4 |
| 362 ± 22 | 8.5 |
| 314 ± 21 | 12.6 |
| 3 ± 16*+ | 12.6 |

Initial Shielded Count Rate/Minute = 11,517 ± 62

Final Shielded Count Rate/Minute = 17 ± 4 (12 ± 3*++)

Thickness of Foil (centimeters) = 0.0104 ± 0.0001

Diffusion Coefficient ($cm^2$/sec) = (16.1 ± 0.5) x $10^{-10}$

*Data used to determine diffusion coefficient.

+Foil counted in a clean tube at end of experiment.

++This is a shielded count that has been corrected as follows:
(12 ± 3) = (8,014/11,517)(17 ± 4).

## APPENDIX B. Chlorine Anneals of Au($^{54}$Mn) Foils

Table 6B. Run 33. 100 Micron $Cl_2$ Anneal of Au($^{54}$Mn) Foil (850°C)

| Count rate/min of foil while in tube | Total time in chlorine (hours) |
|---|---|
| 8,231 ± 66 | zero |
| 4,328 ± 49*+ | 0.6 |
| 2,812 ± 41* | 1.1 |
| 1,858 ± 34 | 1.7 |
| 1,273 ± 30 | 2.3 |
| 365 ± 21 | 6.0 |
| 43 ± 14*++ | 6.0 |

Initial Shielded Count Rate/Minute = 12,906 ± 57

Final Shielded Count Rate/Minute = 55 ± 6 (35 ± 4*+++)

Thickness of Foil (centimeters) = 0.0086 ± 0.0001

Diffusion Coefficient ($cm^2$/sec) = (18.4 ± 0.5) x $10^{-10}$

*Data used to determine diffusion coefficient.

+Foil preheated for 1 hour in hydrogen before admission of chlorine.

++Foil counted in a clean tube at end of experiment.

+++This is a shielded count rate that has been corrected as follows: (35 ± 4) = (8,231/12,906)(55 ± 6).

APPENDIX C. Chlorine Anneals of Au($^{59}$Fe) Foils

Table 1C. Run 30. Low Pressure $Cl_2$ Anneal of Au($^{59}$Fe) Foil (850°C)

| Count rate/min of foil while in tube# | Total time in chlorine (hours) |
|---|---|
| 8,474 ± 68 | zero |
| 7,000 ± 62* | 0.5 |
| 6,431 ± 60* | 1.1 |
| 6,164 ± 59* | 1.6 |
| 5,795 ± 57* | 2.2 |
| 5,052 ± 54* | 3.2 |
| 4,445 ± 51* | 4.2 |
| 4,140 ± 49 | 5.2 |
| 3,689 ± 47 | 6.2 |
| 3,284 ± 44 | 7.2 |
| 2,487 ± 40 | 9.2 |
| 2,051 ± 37 | 10.4 |
| 1,986 ± 36*+ | 10.4 |

Initial Shielded Count Rate/Minute = 11,498 ± 55

Final Shielded Count Rate/Minute = 2,713 ± 31

Thickness of Foil (centimeters) = 0.0102 ± 0.0001

Diffusion Coefficient ($cm^2$/sec) = 3.7

#All counts have been corrected to take into account the half life of $^{59}$Fe (=45 days).

*Data used to determine diffusion coefficient.

+Foil counted in a clean tube at end of experiment.

APPENDIX C. Chlorine Anneals of Au($^{59}$Fe) Foils

Table 2C. Run 23. 100 Micron $Cl_2$ Anneal of Au($^{59}$Fe) Foil (850°C)

| Count rate/min of foil while in tube# | Total time in chlorine (hours) |
|---|---|
| 3,496 ± 47 | zero |
| 2,759 ± 43 | 0.5 |
| 2,027 ± 38 | 1.1 |
| 1,648 ± 36 | 1.6 |
| 1,336 ± 33 | 2.2 |
| 1,051 ± 31 | 3.2 |
| 743 ± 29 | 4.3 |
| 524 ± 27 | 6.0 |
| 328 ± 25 | 8.2 |
| 209 ± 23 | 13.3 |
| 92 ± 22*+ | 13.3 |

Initial Shielded Count Rate/Minute = 4,795 ± 38

Final Shielded Count Rate/Minute = 110 ± 10

Thickness of Foil (centimeters) = 0.0097 ± 0.0001

Diffusion Coefficient ($cm^2$/sec) = $(8.2 \pm 0.5) \times 10^{-10}$

#All counts have been corrected to take into account the half life of $^{59}$Fe (=45 days).

*Data used to determine diffusion coefficient.

+Foil counted in a clean tube at end of experiment.

APPENDIX C. Chlorine Anneals of Au($^{59}$Fe) Foils

Table 3C. Run 26. 100 Micron $Cl_2$ Anneal of Au($^{59}$Fe) Foil (850°C)

| Count rate/min of foil while in tube# | Total time in chlorine (hours) |
|---|---|
| 7,753 ± 65 | zero |
| 5,695 ± 57* | 0.6 |
| 4,737 ± 52* | 1.1 |
| 3,819 ± 48* | 1.7 |
| 3,263 ± 45* | 2.3 |
| 2,767 ± 42* | 2.9 |
| 2,349 ± 39* | 3.5 |
| 2,103 ± 37 | 4.6 |
| 1,582 ± 34 | 6.0 |
| 1,129 ± 30 | 10.6 |
| 930 ± 28 | 12.7 |
| 805 ± 24+ | 12.7 |

Initial Shielded Count Rate/Minute = 11,698 ± 55

Final Shielded Count Rate/Minute = 1,052 ± 24

Thickness of Foil (centimeters) = 0.0089 ± 0.0001

Diffusion Coefficient ($cm^2$/sec) = $(5.6 \pm 0.5) \times 10^{-10}$

#All counts have been corrected to take into account the half life of $^{59}$Fe (=45 days).

*Data used to determine diffusion coefficient.

+Foil counted in a clean tube at end of experiment.

APPENDIX C. Chlorine Anneals of Au($^{59}$Fe) Foils

Table 4C. Run 28. 100 Micron $Cl_2$ Anneal of Au($^{59}$Fe) Foil (850°C)

| Count rate/min of foil while in tube# | Total time in chlorine (hours) |
|---|---|
| 21,700 ± 106* | zero |
| 808 ± 27 | 25.4 |
| 47 ± 19*+ | 25.4 |

Initial Shielded Count Rate/Minute = 33,277 ± 91

Final Shielded Count Rate/Minute = 90 ± 9

Thickness of Foil (centimeters) = 0.0091 ± 0.0001

Diffusion Coefficient ($cm^2$/sec) = 5.7

#All counts have been corrected to take into account the half life of $^{59}$Fe (=45 days).

*Data used to determine diffusion coefficient.

+Foil counted in a clean tube at end of experiment.

## APPENDIX C. Chlorine Anneals of Au($^{59}$Fe) Foils

Table 5C. Run 24. 100 Micron $Cl_2$ Anneal of Oxidized Au($^{59}$Fe) Foil (850°C)

| Count rate/min of foil while in tube# | Total time in chlorine (hours) |
|---|---|
| 3,446 ± 33 | zero |
| 3,133 ± 44 | 0.6 |
| 3,084 ± 43 | 1.1 |
| 3,074 ± 44 | 1.7 |
| 3,006 ± 43 | 2.8 |
| 2,823 ± 42 | 5.3 |
| 2,784 ± 42 | 8.4 |
| 2,794 ± 42 | 11.4 |

Initial Shielded Count Rate/Minute = 4,734 ± 35

Final Shielded Count Rate/Minute = 3,791 ± 31

#All counts have been corrected to take into account the half life of $^{59}$Fe (=45 days).

APPENDIX C. Chlorine Anneals of Au($^{59}$Fe) Foils

Table 6C. Run 32. 100 Micron $Cl_2$ Anneal of Au($^{59}$Fe) Foil (850°C)

| Count rate/min of foil while in tube# | Total time in chlorine (hours) |
|---|---|
| 10,934 ± 76 | zero |
| 6,294 ± 59*+ | 0.5 |
| 4,392 ± 50* | 1.1 |
| 3,208 ± 44* | 1.6 |
| 2,456 ± 40* | 2.2 |
| 496 ± 26 | 6.9 |
| 194 ± 17*++ | 6.9 |

Initial Shielded Count Rate/Minute = 14,422 ± 61

Final Shielded Count Rate/Minute = 216 ± 9 (164 ± 7*+++)

Thickness of Foil (centimeters) = 0.0069 ± 0.0001

Diffusion Coefficient ($cm^2$/sec) = (7.5 ± 0.3) x $10^{-10}$

#All counts have been corrected to take into account the half life of $^{59}$Fe (=45 days).

*Data used to determine diffusion coefficient.

+Admission of chlorine preceded by 1 hour hydrogen anneal.

++Foil counted in a clean tube at end of experiment.

+++This is a shielded count rate that has been corrected as follows: (164 ± 7) = (10,934/14,422)(216 ± 9).