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RADIOACTIVE DECONTAMINATION PROPERTIES OF LABORATORY SURFACES

I. GLASS, STAINLESS STEEL AND LEAD

PAUL C. TOMPKINS
OSCAR M. BIZZELL

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Paul C. Tompkins and Oscar M. Bizzell

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RADIOACTIVE DECONTAMINATION PROPERTIES OF LABORATORY SURFACES

I. GLASS, STAINLESS STEEL AND LEAD

ABSTRACT

The determination of the susceptibility of protective coatings and structural materials to radio-contamination and their subsequent ease of decontamination is essentially a new field but one which the authors feel will become more important in the future. A serious attempt has been made to develop information in such a way that it will contribute to the ultimate construction of standard tables so that decontamination properties may be included among the physical and chemical properties of a material. The primary function of this paper is to establish the basis on which subsequent work is to be reported. Materials used for these preliminary studies were glass, polished stainless steel, unpolished stainless steel and lead. The effectiveness of various reagents in removing radio-contamination from these materials is listed in Tables I - IV, and a "standard" reagent for the removal of P^{32}, Ba^{140}-LA^{140} and I^{131} is selected. The degree of decontamination necessary in order to work safely at various levels of activity is listed in Table V. As a basis for comparing other products, the standard values achieved on these generally accepted structural materials are listed in Table VI.

[redacted]

RADIOACTIVE DECONTAMINATION PROPERTIES OF LABORATORY SURFACES

I. GLASS, STAINLESS STEEL AND LEAD[1]

Paul G. Tompkins[2] and Oscar M. Bizzell[3]
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One of the major problems faced in the construction of radiochemical facilities is the selection of structural materials and surface coatings which permit ready cleaning. The requirements for a decontaminable surface[4] which have become accepted among Atomic Energy Commission workers may be listed as follows:

1. Smooth and nonporous (minimum of adsorption area and penetration)
2. Nonionic (minimum exchange)
3. Resistant to corrosion by acids, alkalis, organic solvents
4. Resistant to heat

These points are the major criteria that relate to the properties of the materials themselves. Many other pertinent points such as cost, durability, and the manner of construction (no cracks, etc.) have been suggested in more extensive discussions of the subject (1,2,3,4). It is the purpose of this paper to report preliminary studies made on the decontamination of glass, polished stainless steel (type 347), unpolished stainless steel (type 316), and lead, since they are always mentioned among the materials usually suggested for radiochemical facilities (6,7). These experiments have led to the development of tests by which the suitability of different materials and cleaning reagents for use in laboratories working with P^{32}, Ba^{140}, and I^{131} may eventually be estimated.

Relatively minor defections such as scratches, etc., (1,3,4) on the surface result in relatively large variations in both the susceptibility of the surface to contamination and its subsequent ease of decontamination. Therefore,

[redacted]

an effort was made to select materials that were representative of the optimum conditions that might reasonably be expected under normal laboratory conditions. Further experience under a variety of working conditions must be gained before a true evaluation can be made. Meanwhile, it is hoped that a body of standardized data can be built up which, in conjunction with known chemical, structural and thermal properties, will aid in the selection of surface materials used in radiochemical laboratories.

MATERIALS

NUCLIDES.

The nuclides were carrier-free(5) $H_3P^{32}O_4$ in HCl solution (pH 2-3), $Ba^{140}Cl_2$ in HCl solution (pH 2-3) and NaI^{131} in $NAHSO_3$ solution (pH-8). P^{32} and I^{131} are used in biological and medical work, while Ba^{140} resembles calcium. This combination also permits differences between anions and cations to be studied. The active solutions were isotope shipments as received from the Oak Ridge National Laboratory (8). Approximately 100 - 200 μc of activity was applied as contamination in each case.

REAGENTS

Acid reagents were prepared by diluting the appropriate volume of the concentrated C. P. acid with distilled water. Other reagents were prepared by dissolving the solid material in distilled water and diluting to 100 ml. Thus 10% T.S.P. indicates that there are 10 g. Na_3PO_4 per 100 ml. of solution.

PLAQUES

The materials for decontamination tests were prepared by cutting 2.5 x 2.5-inch squares from a 0.05 - 0.125-inch-thick sheet of material to be tested. The plaques were cut in half for the adsorption tests, giving strips 1.25 x 2.5 inches. The edges were smoothed to minimize adsorption.

METHODS FOR TESTING

AIR DRIED CONTAMINATION

The plaques were contaminated by pipetting 0.1 ml. of the active solution onto the center of the area. A one-inch funnel was mounted in such a position that it could be lowered over the drop of solution to within a few millimeters of the plaque, (Fig. I). A vacuum was applied through a filter to the stem of the funnel. The air flow through the funnel was adjusted to a velocity which prevented the solution from flowing near the rim of the funnel. At this rate, it was possible to evaporate the solution to dryness in approximately one hour.

The 0.1-ml. sample contained around 5 µg. total solids. The solution spread over an area of <1 cm^2 on nonwetting surfaces to as much as 2 cm^2 on an easily wet surface. Therefore, the general solid distribution was about 1 - 10 µg./cm^2 of surface.

ADSORPTION TESTS

The susceptibility of a surface toward contamination by a particular ion is indicated in part by the adsorption of that ion from an aqueous medium. One tenth (0.1) ml. of the active solution was pipetted onto the surface about 3/4 inch from the end of a 1.25 x 2.5-inch plaque. The entire plaque was covered by an inverted watch glass and allowed to stand for 1 hour, after which the solution was carefully sucked off with a transfer pipette. The plaque was washed immediately by immersion in 4 successive 30-ml. volumes of water in a 50-ml. beaker for 5 second each. It was then soaked 10 minutes in a fifth 30-ml. volume of water after which it was dried over $CaSO_4$ before monitoring.

The percentage of the radionuclide adsorbed was calculated from the equation:

$$\text{Percentage adsorbed} = \left(\frac{\text{Activity adsorbed}}{\text{Activity applied}}\right) \times 100 \qquad \text{Equation 1}$$

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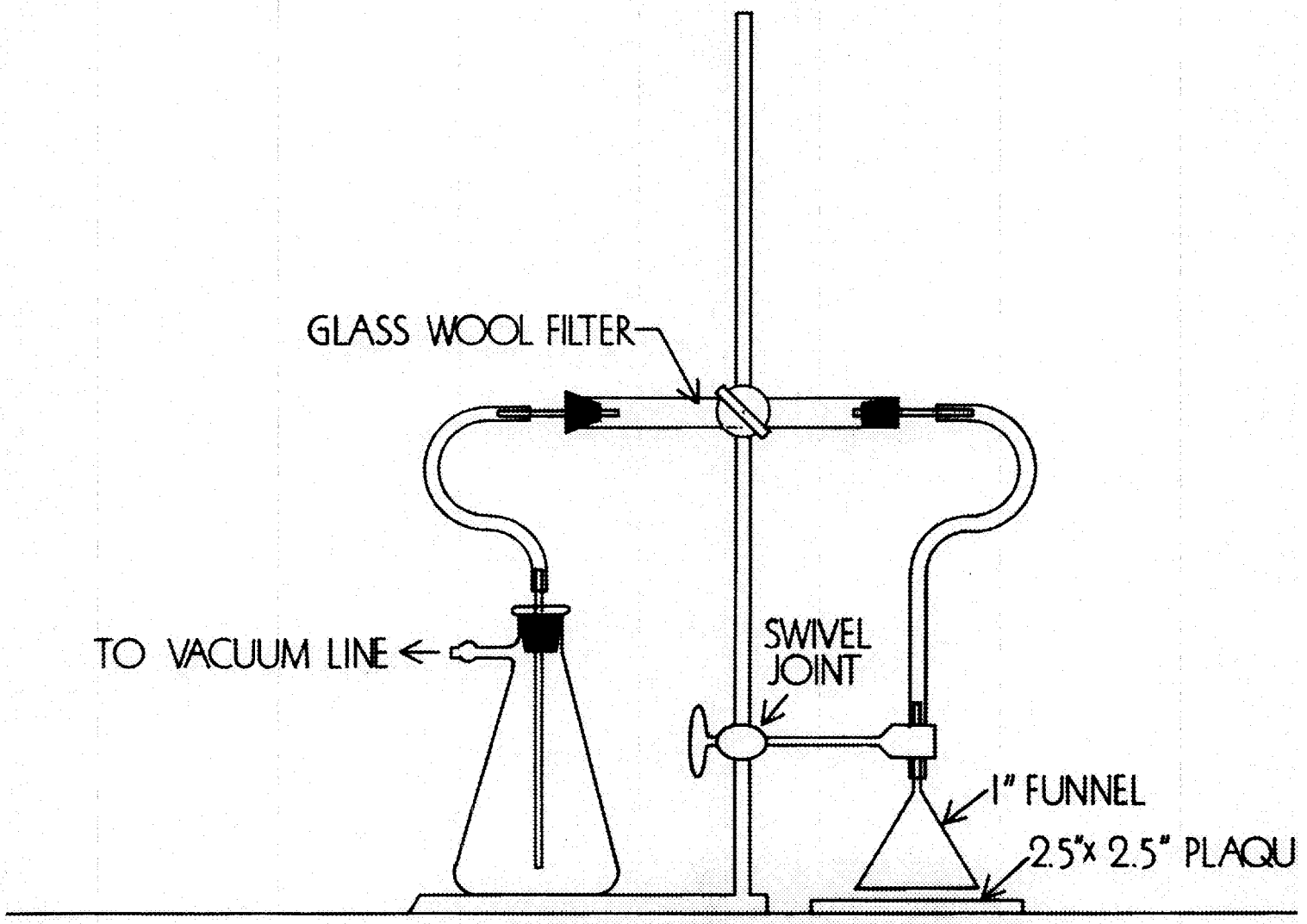

FIGURE I — DRYING UNIT

This equation was derived from the more general equation:

$$\text{Percentage adsorbed/cc/cm}^2 = \left(\frac{\text{Activity adsorbed/cm}^2 \text{ of surface}}{\text{Act./cc. sol. applied x cc/cm}^2 \text{ surface covered}}\right) \times 100 \quad \text{Eq}$$

Under the conditions used, the activity per cc. of the solution applied was directly proportional to the total activity since a constant volume was used throughout. Also, the area contaminated was identical with the area covered by the solution so that Equation 2 reduces to Equation 1.

DECONTAMINATION

A stepwise decontamination procedure similar to that used in laboratory cleaning was used for much of this work. Reagent decontamination without scrubbing (Step 1) was used first to lower the activity level as much as possible before personnel exposure became necessary. One-fourth (0.25) ml. of the reagent was applied to the affected area and allowed to stand approximately 3 minutes. When two different reagents were applied, an approximately equal volume of each was used, the total reagent volume remaining constant. The plaque was rinsed with a spray of water, blotted dry, and monitored. Each subsequent attempt at decontamination (Steps 2, 3, etc.) was accomplished by applying 2 ml. of reagent, and brushing manually with a 1.5 x 1.5-inch surgical brush for 1 minute. Radioautographs have demonstrated that the activity was rather uniformly spread over the contaminated area, and that less than 1% of the activity spread to other portions of the plaque during the brushing process (9).

The data are reported in terms of the decontamination index, D.I.:

$$\text{D.I.} = \log \left(\frac{\text{Activity on surface before cleaning}}{\text{Activity on surface after cleaning}}\right)^{(6)} \qquad \text{Equation 3}$$

Since the area covered by the radionuclide was unchanged by the cleaning process, the decontamination index represents the fraction of the radionuclide removed per unit of surface area.

MONITORING

The plaques were monitored with an end-window Geiger-Mueller tube enclosed in a lead shield with standard shelf positions, and a scaler equipped with a scale of 1024. The plaque was placed on a 2.5 x 3.25-inch card, and inserted into one of the shelf positions in the lead shield. A new card was used for each determination to minimize the probability of contaminating the inside of the lead shield. When the range of the G-M tube was exceeded, the activity was determined in an ionization chamber by comparison with a control of known activity mounted under the same conditions.

RESULTS AND DISCUSSION

ADSORPTION TEST

The adsorption test described in the experimental section is used to investigate the susceptibility of the various surfaces to contamination; that is, the extent to which the radioelement becomes attached to the surface. The method by which the attachment occurs is immaterial. The radioelement, in the general case, may be held by chemisorption (e.g. ion exchange) with surface valences, by physical adsorption or mechanical means (diffusion into cracks and pores on the surface). The form in which the radioelement occurs on the surface (i.e., ionic or colloidal aggregates) depends largely on the composition of the medium from which it is deposited.

Since the radioelements exist as ions in the solutions used as the contaminating medium for this work, and since the surface materials were selected because they provide a relatively small specific surface area, ion exchange and chemisorption are the predominant phenomena in the particular studies reported here.

The results are shown in Table VI.

Several tests with different shipments of the carrier-free isotopes as received from Oak Ridge showed that the percentage adsorbed from different solutions of the same element varied by a factor of 2 or 3. The carrier-free samples were used because they represent the highest dilutions of the element likely to be met and should give the highest percentage adsorption. Except for the fact that the adsorption of Ba^{140} - La^{140} on lead was unexpectedly high, the comparative figures for each element on Pyrex glass, polished stainless steel, unpolished stainless steel and lead seem reasonable.

The general similarity between glass and polished stainless steel has been known for some time, and is usually attributed to the very smooth surface which they present. The difference between polished and unpolished stainless steel probably reflects the relative specific surfaces of the two materials more than differences in composition.

The increasing value for $H_3P^{32}O_4$ between glass and lead as well as the higher adsorption of I^- on Pb as compared to I^- on glass or either variety of stainless steel was anticipated on the basis that the formation of insoluble salts should increase the apparent adsorption.

Since the procedure used to derive the adsorption figures has been adopted in our laboratory as a routine test for the susceptibility of different materials to contamination, it seems worth while to consider its derivation in greater detail.

Separation of porous from nonporous surfaces by this procedure is not difficult. Several preliminary experiments demonstrated that the susceptibility of a porous surface to contamination by a solution was reflected by an apparent adsorption of greater than 1%. The nonporous materials for which we were looking should take up much less than 1%, often 0.01% or less, except when specific chemical reactions occur between the surface material and the radioelement in the solution.

A one-hour contact time seemed sufficient to classify (within an order of magnitude) the relative adsorptive power of nonporous materials because of the general character of the adsorption isotherms which are followed.

To illustrate, a typical curve for the adsorption of $H_3P^{32}O_4$ on frosted glass[7] (see Fig. 2) has been chosen as the basis for discussion since this system will be used later in the report to show the basic principles of the subsequent decontamination cycle. In this experiment, the frosted end of a microscope slide was immersed in a solution of $H_3P^{32}O_4$, removed at intervals, rinsed in successive changes of distilled water and monitored.

It should be noted that a very rapid phase of adsorption deposited an amount equivalent to a few tenths to a few per cent of the ultimate equilibrium amount of P^{32} within a matter of seconds after the solution and surface were brought together. This is a typical feature of the adsorption of polar ions on different surfaces and is attributed to electrostatic adsorption or ion exchange at the outer surface of the electric double layer at the solid-solution interface (10).

Two slower phases of adsorption were found when the isotherm in Figure 2 was replotted as log (1-F) versus time where F is the fraction of the equilibrium[8] value. These phases were represented by two straight lines with half times of 10 minutes and 9 hours. The 10-minute step was essentially complete after the first hour, the total activity at this time being about 25% of the equilibrium value. In the adsorption of polar ions, such steps commonly follow the rapid initial adsorption at the surface of the double layer and are usually attributed to successive steps, one of which is probably due to diffusion of the radioelement through the double layer (10,11).

The fact that the semilog plots were straight lines, of course, indicates an exponential equation for the lines. This is in accord with the

Figure 2

ADSORPTION OF P^{32} ON GLASS

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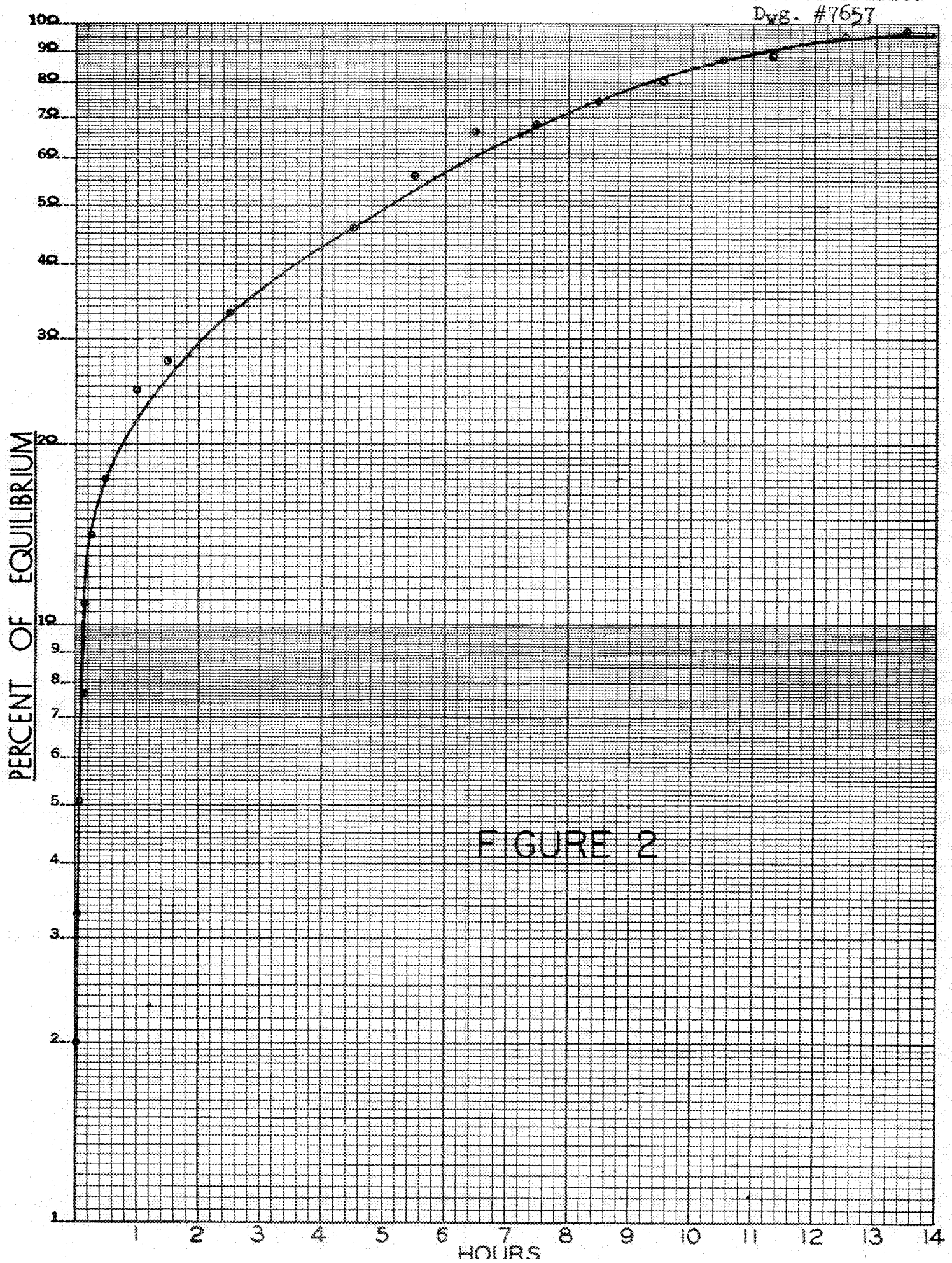


FIGURE 2

observation of Boyd et al., that an exponential equation is obtained when the reaction kinetics of the exchange occurring between a solution and an ion exchange resin is calculated for either a diffusion controlled or a chemical exchange mechanism (12). An exponential equation is also obtained for the exchange between a radionuclide and its stable isotopes in the same ionic form when the stable ion is initially in exchange equilibrium in two or more compartments, and the radionuclide is introduced into one of them (13,14). Because of the widespread occurrence of stepwise exponential adsorption (10,11,12,13,14) it is logical to expect that adsorption quite generally will show initially rapid with later slower stages and that each stage will be exponential in character, i.e., the form of the adsorption curve observed in this experiment will prove to be the rule rather than the exception for the adsorption conditions used in these studies.

By selecting an "adsorption" time of one hour one is making comparisons at a time when the adsorption is proceeding rather slowly although only around 10 to 25% of the equilibrium distribution may have been reached. A more exact comparison at a later time is not necessary because the important point to the laboratory worker is the ratio of the adsorbed activity to the "tolerance" activity permitted on the surface. For example, if the maximum activity permitted on a given surface is 100 c/m with a particular instrument, and the maximum activity which can be adsorbed is 10^6 c/m, about 10^4 c/m will be taken up in a matter of seconds. This will rise to about 2 or 3 times 10^5 c/m during the first hour. When one is choosing between two possible materials, it makes little difference if one must reduce 10^6 c/m to 100 or 5×10^5 c/m to 100. The two must differ by a factor of 10 or more before one surface has a real practical advantage over the other. A difference this large can be identified by the one-hour test.

DECONTAMINATION

The results of the decontamination test described in the section on experimental procedures are given in Tables I - IV. The tests were run in duplicate and were repeated in several instances with different shipments of the radioelement. The over-all precision obtained was ± 0.3 decontamination index units. Several observations of interest are evident in the general pattern of the results.

The most consistent feature is the fact that the cleaning action of any reagent is, for all practical purposes, completed at the end of the second step in the decontamination procedure. Also, the first figure of the decontamination index (i.e., the exponent of the decontamination factor) is set at this time, and further attempts to reduce the contaminant on the surface are relatively unprofitable. Thus, it can be found almost at once if the decontamination index on any particular plaque is going to be 2, 3, or 4, etc.

Less consistently observed, but equally interesting is the fact that the indices for the efficiency of a variety of reagents used on some surfaces are remarkably similar. For example, the decontamination index for all three elements on Pyrex glass is around 4, regardless of the cleaning reagent selected.

Finally, there is no striking benefit demonstrable from the presence in the reagent of carrier isotopic with the radioelement on the surface. Those effects which were observed were far less than they should be if the radioisotope were exchanging significantly with the carrier in the cleaning reagent.

These results, as well as some of the finer points, are qualitatively explainable by a simplified picture of the decontamination process. One

TABLE I

REMOVAL OF AIR-DRIED CONTAMINATION FROM PYREX GLASS BY STEPWISE PROCEDURE

Isotope	Reagent	D. I. Per Step					Total D. I.	
		Step 1	Step 2	Step 3	Step 4	Step 5	Initial Reagent	All Reagents
P^{32}	1% Mulsor 224	2.9	1.5	0.23	(>2.5)[1]	—	4.6	>7.0
	3N HNO_3-3N H_3PO_4	3.6	0.6	0.25	0.11	0.08	4.6	4.6
	Satd. Calgon	3.0	1.0	—	—	—	4.0	4.0
	6N HNO_3	3.4	0.4	0.3	0.13	(>2.7)[1]	4.2	>7.0
	1% Sapamine	2.7	0.4	—	—	—	3.1	3.1
Ba^{140}	1% Sequestrene	1.9	2.1	0.5	0.4	—	4.9	4.9
	6N HNO_3	2.8	1.3	(0.1)[2]	—	—	4.1	4.2
	1% Mulsor 224	1.9	1.8	0.2	(0.3)[3]	—	3.9	4.2
	10% Amm. Cit.	2.5	0.6	(0.15)[4]	(>2.7)[1]	—	3.1	>6.0
I^{131}	56% HI	4.1	0.9	0.3	—	—	5.3	5.3
	10% $NaHSO_3$ Satd. KI	3.5	1.0	0.18	(0.2)[4]	—	4.7	4.9
	1% Sapamine	3.0	1.1	0.11	(0.8)[5]	—	4.2	5.0
	Satd. $NaHSO_3$	3.2	0.8	0.2	(0.33)[3]	—	4.2	4.5

1. Reagent changed to 5% $NH_4F.HF$ which dissolves the surface layer
2. Reagent changed to 10% Ammonium Citrate
3. Reagent changed to Chromic Acid Cleaning Solution
4. Reagent changed to 6N HNO_3
5. Reagent changed to 16N HNO_3

TABLE II

REMOVAL OF AIR-DRIED CONTAMINATION FROM
POLISHED STAINLESS STEEL
BY STEPWISE PROCEDURE

Isotope	Reagent	D. I. Per Step					Total D. I.	
		Step 1	Step 2	Step 3	Step 4	Step 5	Initial Reagent	All Reagents
P^{32}	3N HNO_3-3N H_3PO_4	2.7	0.5	0.04	(1.5)[1]	0.6	3.2	5.3
	6N HNO_3	2.3	0.4	0.3	—	—	3.0	3.0
	1% Sapamine	2.3	0.23	(0.8)[2]	0.3	0.3	2.5	3.9
Ba^{140}	6N HNO_3	5.0	0.7	—	—	—	5.7	5.7
	10% Amm. Cit. 10% NaOH	2.3	1.1	0.6	(0.2)[3]	0.18	4.0	4.4
I^{131}	56% HI	4.7	1.8	—	—	—	6.5	6.5
	6N HNO_3 10% $NaHSO_3$	2.7	2.5	—	—	—	5.2	5.2

1. Reagent changed to Conc. HCl

2. Reagent changed to 6N HCl

3. Reagent changed to 1% Sequestrene

TABLE III

REMOVAL OF AIR-DRIED CONTAMINATION FROM UNPOLISHED STAINLESS STEEL BY STEPWISE PROCEDURE

Isotope	Reagent	D. I. Per Step*					Total D. I.	
		Step 1	Step 2	Step 3	Step 4	Step 5	Initial Reagent	All Reagents
P^{32}	6N HNO_3	<2.0	0.6	(0.5)1	0.2	—	2.6	3.3
	3N HNO_3-3N H_3PO_4	<2.0	0.5	0.0	—	—	2.5	2.5
	1N HCl	<2.0	0.5	(0.0)2	—	—	2.5	2.5
	1% Mulsor 224	<2.0	0.3	(0.7)3	0.6	—	2.3	3.6
Ba^{140}	6N HNO_3	2.8	1.1	0.04	—	—	3.9	3.9
	6N HCl	2.3	1.1	(0.5)3	—	—	3.4	3.9
	1% Sequestrene	<1.8	0.6	(1.5)4	—	—	2.4	3.9
	10% Amm. Cit.	<1.8	0.3	(0.3)2	—	—	2.1	2.4
I^{131}	56% HI	3.8	1.1	0.3	0.3	0.0	5.5	5.5
	10% NaOH 10% $NaHSO_3$	2.7	1.0	(0.4)5	—	—	3.7	4.1
	10% $NaHSO_3$ Satd. KI	3.2	0.5	(0.7)4	0.19	0.08	3.7	4.7
	6N HCl	2.0	1.0	(0.3)3	—	—	3.0	3.3

1. Reagent changed to 6N HCl
2. Reagent changed to 5% $NH_4F.HF$
3. Reagent changed to Conc. HCl
4. Reagent changed to Conc. HNO_3
5. Reagent changed to 6N HNO_3

* The ionization chamber was not available at this time. The activity was close to the upper limits for the G. M. tube.

TABLE IV

REMOVAL OF AIR-DRIED CONTAMINATION FROM LEAD BY STEPWISE PROCEDURE

Isotope	Reagent	D. I. Per Step					Total D. I.	
		Step 1	Step 2	Step 3	Step 4	Step 5	Initial Reagent	All Reagents
P^{32}	3N HNO_3-3N H_3PO_4	2.8	2.0	0.4	—	—	5.2	5.2
	6N HCl	2.7	1.5	(0.27)[1]	—	—	4.2	4.5
	6N HNO_3	2.6	1.1	(0.34)[2]	—	—	3.7	4.0
	10% Na_3PO_4	<2.0	0.3	0.3	—	—	2.6	2.6
Ba^{140}	6N HNO_3	3.2	1.0	0.8	—	—	5.0	5.0
	Conc. HNO_3	2.0	1.9	1.0	—	—	4.9	4.9
	6N HCl	<1.7	1.0	0.0	—	—	2.7	2.7
	10% Amm. Cit.	2.0	0.4	0.3	—	—	2.7	2.7
I^{131}	56% HI	3.0	1.1	0.2	0.1	—	4.4	4.4
	6N HCl	<2.0	0.3	0.3	0.0	—	2.6	2.6
	1% Sapamine	<2.0	0.3	(0.7)[1]	0.3	—	2.3	3.3
	1% $NaHSO_3$ Satd. KI	<2.0	0.3	—	—	—	2.3	2.3

1. Reagent changed to Conc. HNO_3

2. Reagent changed to 5% $NH_4F.HF$

would expect that the first action of a liquid reagent would be to simply dissolve any salts of the radioelement that might be lying loose on the surface. Another immediate action would be the rapid adsorption of solute ions originally present in the cleaning solution, and exchange between the surface and solution where such exchange is possible.

Part of the cleaning effect will depend on how fast these ions can reach the surface, and on the degree to which they can react with the surface valences in competition with the ions of the radioelement. Thus, the effect of acids is primarily due to the H^+ and secondarily due to the anion.

The radioelement will ultimately become distributed between the solution and the surface in the proportions determined by its distribution coefficient between the cleaning solvent and the material. However, the rate at which the equilibrium is attained might well follow an exponential law since the various rate equations mentioned in connection with adsorption hold for both adsorption and desorption steps. If a diffusion process (e.g., diffusion from micropores) is involved in the decontamination, a slow rate of exchange could easily result because of rapid replacement of solution would not occur at the sites of contamination deep in the pores.

Regardless of the explanation, if the exchange rate were slow enough, it would appear as if the radioelement were irreversibly attached to the surface. It would also account for the repeated observation that isotopic carrier contributes far less to the displacement of the radioelement than one might expect from its concentration in the reagent.

Two experiments were, therefore, set up to determine the extent to which exchange rates might be important in the reagent decontamination process. In the first experiment, some of the slides which had been equilibrated with a P^{32} solution for the adsorption experiments were then cleaned

by immersion in 500 ml. of a 3N HNO_3 - 3N H_3PO_4 solution which was continuously agitated. In the second experiment, slides on which the P^{32} had been allowed to dry overnight over $CaSO_4$ were cleaned by the same procedure. The slides were removed at intervals, rinsed, dried and monitored.

The results of these two experiments are shown in Figure 3. In the first experiment, about 98% of the adsorbed activity was removed during the first 10 minutes. The activity then came off with a half-time of about 70 minutes followed by a third step with a half-time of around 9 hours. Practically all the desorption obtained during the 15-hour run was obtained during the first 6 hours at which time the decontamination index was 2.4 as compared to only 2.7 at 15 hours. The fact that the 9-hour slope was not altered by changing to fresh reagent proves conclusively that the exchange rate was the limiting factor, and that the position of the ultimate equilibrium had little or no influence on the rate at which the P^{32} atoms were removed from the glass. If one needs to remove, in a short time, 99.9% of the activity remaining after 6 hours, it will be necessary to attack the surface itself.

The second experiment on air-dried material changes none of the essential conclusions of the preceding discussion. In this case, the decontamination index was 3.0 after 2 hours immersion, and only 3.2 after 15 hours. The difference between the two experiments was established in the first few minutes just as it was in the adsorption cycle. It should be noted in passing, that frosted glass was used for the first experiment, and smooth, plate glass for the second.

The striking similarity in the results obtained by the stepwise procedure is illustrated in Figure 4. The same materials and cleaning reagents were used.

Figure 3

DESORPTION OF P^{32} FROM GLASS BY IMMERSION IN 3N HNO_3-3N H_3PO_4

Not Classified
Dwg. #7658

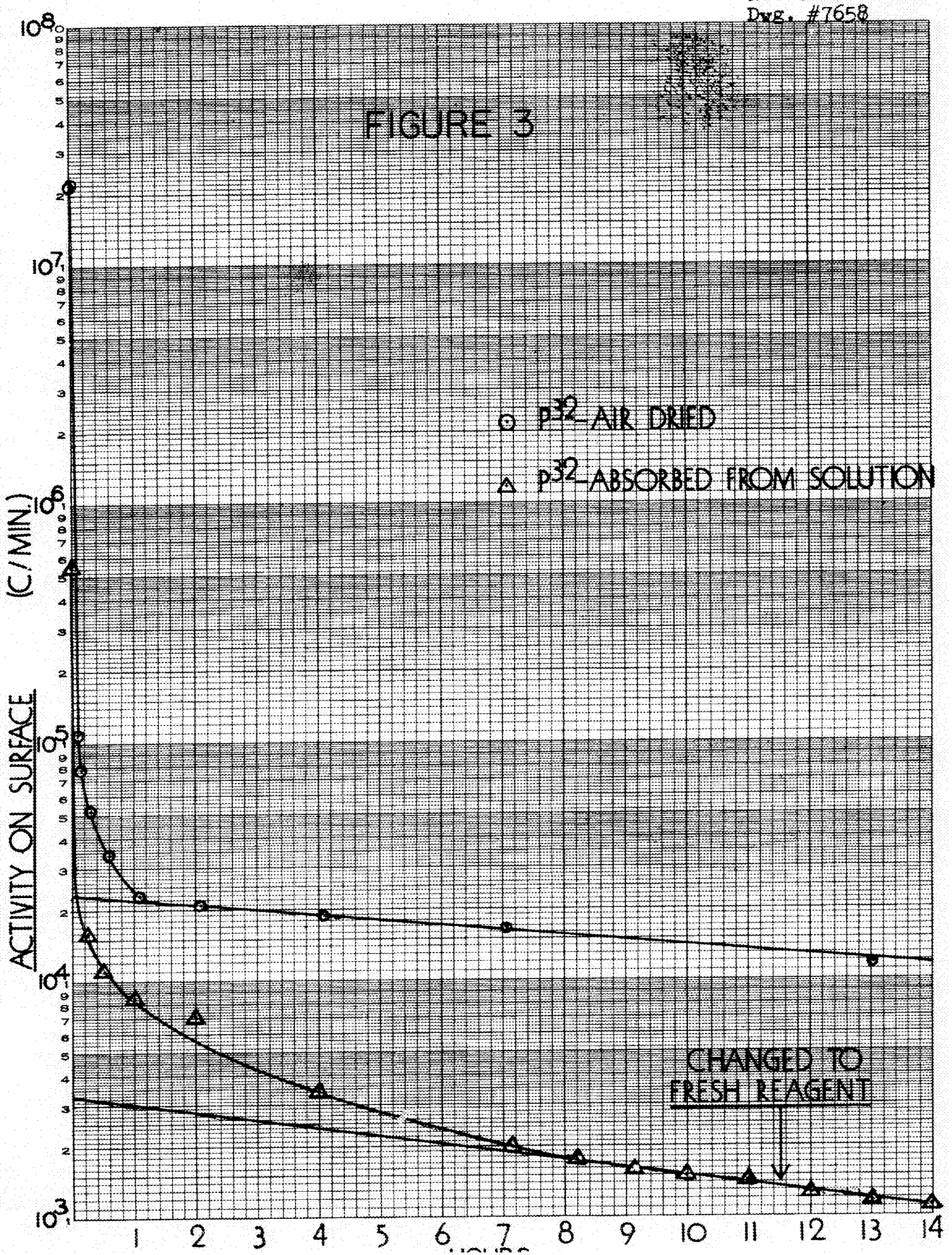
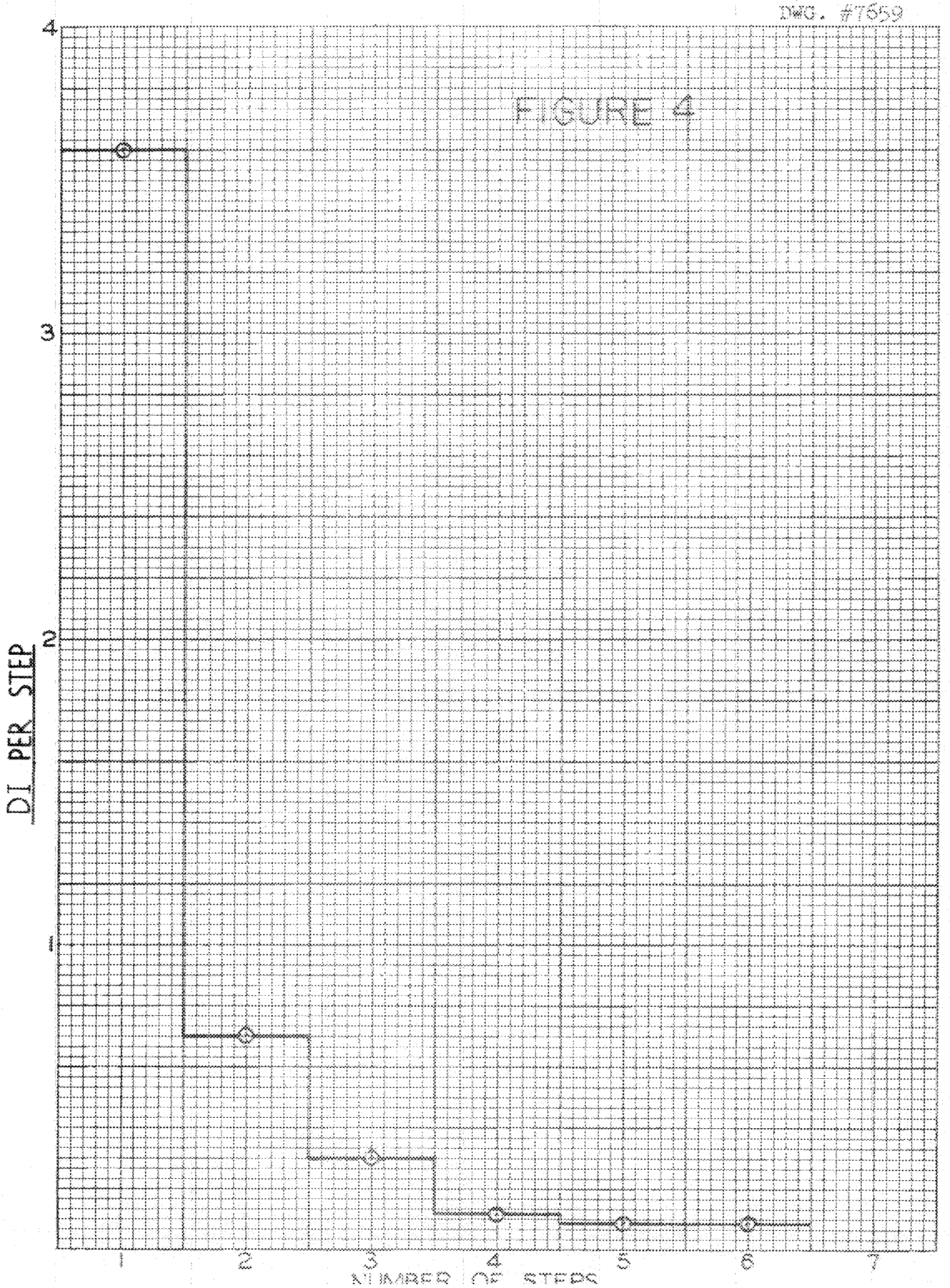


Figure 4

TYPICAL STEPWISE DECONTAMINATION SEQUENCE; P^{32} FROM PYREX GLASS WITH 3N HNO_3-3N H_3PO_4

Not Classified
DWG. #7659



The essential conclusion to be drawn from these data is that the decontaminability of a given surface with a particular reagent when dissolution of the surface is not involved, is controlled almost completely by that fraction of the activity that can be removed in a short time. This fraction may be logically assumed to consist of ions which have not reacted with surface valences at all, or those which are loosely bound to the outer atoms of the double layer surrounding the surface. Accordingly, detergents are often as good decontaminating agents as are stronger reagents. The widespread use of such reagents as complexing agents and isotopic carrier which displace the equilibrium in the direction of the solution is based on an erroneous conception of the cleaning mechanism. These reagents only influence the distribution of the loosely held fraction between the surface and cleaning solvent and prevent readsorption of radioactive atoms.

It is clear that the stepwise decontamination test actually measures that fraction of the total nuclide present as a contaminant which reacts with or diffuses into the surface prior to the cleaning operation, and therefore cannot be readily removed. The size of this fraction can be established by carrying the stepwise decontamination procedure through only the first two steps.

This procedure, therefore, makes it possible to compare the operation of any one variable if the other important variables can be controlled. The important variables are: (1) the surface material, (2) the contaminating conditions, and (3) the cleaning reagent.

Some standardization has already been achieved in the selection of the surfaces to be tested, the composition of the solutions used as the contaminating reagent, and the manner of its application. It is still necessary to select a "standard reagent" if either different surfaces or contaminating

conditions are to be surveyed systematically. An examination of Tables I - IV indicates that no single cleaning reagent is outstanding for all the elements on all the surfaces. However, with each element, there is at least one reagent which appears well up on the efficiency list of reagents for the removal of that element from each of the four different materials. Therefore, a "standard reagent" has been selected for each element as follows:

For P^{32}: 3N HNO_3 - 3N H_3PO_4

For Ba^{140}: 6N HNO_3

For I^{131}: 56% HI

Although one would hardly expect to use these particular reagents regularly for cleaning floors and tables, they do provide a standard against which milder reagents (e.g., detergents) can be compared as well as a standard through which other selected variables may be compared.

It should be pointed out that, as is shown in Table I, $NH_4F.HF$ is the most effective cleaning reagent known for glass. Project experience has demonstrated that when judiciously used there is no recognizable resulting damage (15).

The drying time required to give reproducible contaminating conditions was determined by the two-step procedure with the standard reagents using plaques that had been stored for different lengths of time. On the basis of these results, shown in Figure 5, a standard drying time of 18 to 24 hours was selected.

SYNTHESIS OF THE RESULTS

The preceding discussion and data make it possible to begin the task of standardizing the necessary information. A comparison of different materials is desired with respect to two broad situations. One is the problem of cleaning an area, such as a hood, where the contamination will occur primarily through

Figure 5

EFFECT OF DEHYDRATION ON DECONTAMINATION OF P^{32}

Not Classified
Dwg. #7660

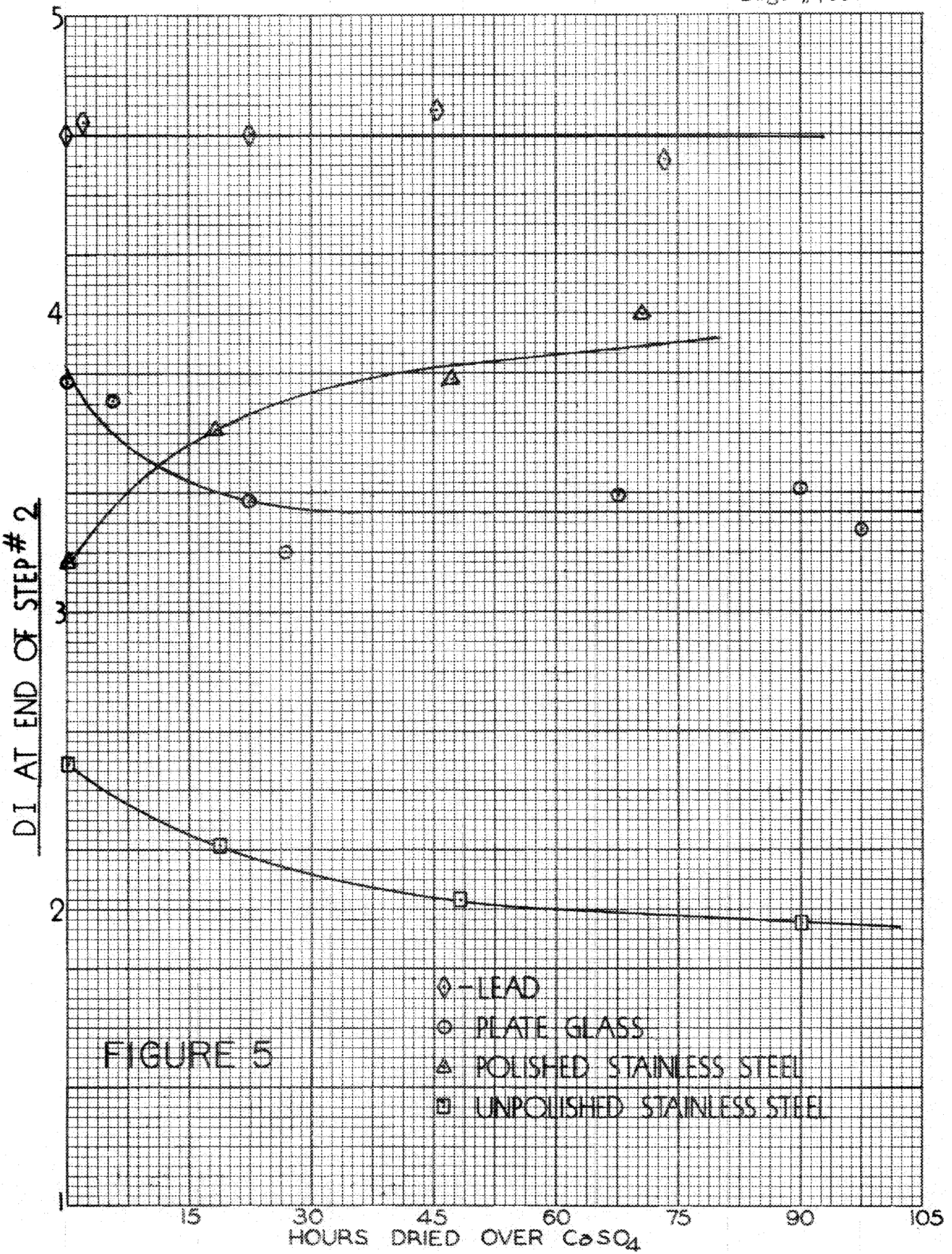


FIGURE 5

small drops which have subsequently dried. The other is an evaluation of how much activity is likely to remain after a major accident or spill has occurred and the surface has been cleaned within a short time (an hour or less) afterwards.

For comparison of materials, it is necessary to obtain a decontamination index. This index must be obtained under conditions which have been standardized with respect to the contaminating conditions (i.e., element, composition and form of the contaminating medium, and method of application) and also with respect to the process of cleaning (i.e., reagent and procedure used). The $\log\left(\frac{\text{activity on surface before cleaning}}{\text{activity on surface after cleaning}}\right)$ obtained under such standard conditions may be called a "standard" decontamination index ($D.I._S$). The authors tentatively propose that $D.I._S$ for the removal of a particular element from a given material be defined as that decontamination index which is obtained at the end of the second step in the stepwise cleaning procedure when the contaminant has been dried on the surface at room temperature for 18 - 24 hours and the surface subsequently cleaned with the "standard reagent" for the radioelement in question.

In evaluating the second case (i.e., a spill) it is desirable to not only compare different materials, but also to estimate how much activity will be left after the cleaning process. The most accurate procedure would be to remove the activity retained by the adsorption test, and obtain the ratio of activity left after the cleaning procedure to the total activity applied in the initial contaminating solution. This method is technically impractical because it would require the use of very "hot" initial solutions to leave enough activity at the end to get an accurate count. Therefore, an estimate of the desired ratio has been obtained indirectly from the percentage adsorption and the standard decontamination index in the following way:

$$\left(\frac{\text{Act. after cleaning spill}}{\text{Total act. of sample}}\right) = \left(\frac{\text{Act. adsorbed}}{\text{Total act. of sample}}\right) \times \left(\frac{\text{Act. after cleaning}}{\text{Act. before cleaning}}\right) \quad \text{Eq. 4}$$

$$= \left(\frac{\text{Fraction adsorbed}}{\text{Decontamination factor}}\right) \quad \text{Equation 5}$$

If this equation is written in the logarithmic form, it becomes:

$$\log \left(\frac{\text{Act. after cleaning spill}}{\text{Total act. of sample}}\right) = \log \text{fraction adsorbed} - \text{D.I.}_{\text{Ads}} \quad \text{Equation 6}$$

where D.I._{Ads} is the index obtained from the surface contaminated by adsorption.

The term on the right side of Equation 6 will always be negative. Therefore, the authors propose that a new term, called the spill index (S.I.) and defined as $-\log \left(\frac{\text{Act. after cleaning}}{\text{Total activity}}\right)$ be introduced as a measure of the situation that would be created in case of an accident.

The only decontamination index available is that obtained from the use of the air-dried contaminating test, whereas the one that should be used here would be obtained from applying the contaminant by adsorption. From Figure 3, and other experiments, it has been estimated that the proper index would usually be 1 to 2 units less than that obtained by the air-drying procedure. Therefore, to a rough approximation, the D.I._{Ads} is simply two units less than D.I._{S}. The same numerical result is obtained from Equation 6 if the fraction adsorbed is expressed as the percentage adsorbed and the logarithm of this value is computed. This, in effect, adds 2 units to the logarithm of the fraction adsorbed and a value for the spill index may be calculated directly from the results of Tables I-IV by the equation:

$$\text{Spill Index (S.I.)} = -(\log \%\ \text{ads.} - \text{D.I.}_{\text{S}}) \quad \text{Equation 7}$$

Thus from Table VI, the percentage adsorption of I^- by unpolished stainless steel is 0.06%, and the standard decontamination index is 4.9. Therefore, the spill index for iodine with unpolished stainless steel is -(-1.2 - 4.9) or 6.1. Thus, if one spilled a sample containing 10 mc. I^{131} on this surface, he might expect to find about 0.01 μc. I^{131} left firmly attached to the surface if the spill were cleaned up in one hour or less using a reagent as effective as 56% HI.

The schedule presented in Table V has been used to estimate the spill index and the standard decontamination index that a material should have for work at different levels of activity. If the frequency of work at high levels is low, a less satisfactory material can be economically used because the probability of serious contamination is less and one can afford to utilize surface erosion for the ultimate cleaning occasionally. These values should be interpreted as representative of what the base material itself can achieve. Superficial coatings of various kinds can be used to raise the activity capable of being handled adequately by the base material.

The data for Pyrex glass, lead, polished stainless steel # 347, unpolished stainless steel # 316, and two additional stainless steel samples # 302 have been summarized in Table VI. The authors consider that a difference of 0.5 units in either the spill index or standard decontamination index is probably significant, and that a differerence of 1 unit is certainly significant. Less specificity toward the radioelement is shown by Pyrex glass than by either lead or stainless steel. All of the stainless steels are less satisfactory when used in conjunction with P^{32} than with Ba^{140} or I^{131}. Also, some specificity with respect to the type of stainless steel is shown toward both barium and iodine.

The high standard decontamination index observed on lead is due primarily

TABLE V

APPROXIMATE SPILL INDICES (S.I.) FOR DIFFERENT LEVELS OF ACTIVITY

Approximate Level	S. I.	D. I.
Less than 1 μc	~3	2
1 μc - 1 mc (Low Frequency)	5 - 6	3 - 4
1 μc - 1 mc (High Frequency)	7 - 8	5 - 6
1 mc - 100 mc (Low Frequency)	7 - 8	5 - 6
1 mc - 100 mc (High Frequency)	9 - 10	7 - 8
100 mc - 1 C (Low Frequency)	9 - 10	7 - 8
100 mc - 1 C (High Frequency)	11 - 12	9 - 10

TABLE VI

STANDARD DATA ON SUSCEPTIBILITY AND CLEANING PROPERTIES OF GLASS, STAINLESS STEEL, AND LEAD

Material	Isotope	Spill Index (S.I.)	Percent Adsorbed in One Hour	$D.I._s$
Pyrex Glass	P^{32}	5.9	0.02	4.2
	Ba^{140}	4.8	0.2	4.1
	I^{131}	6.4	0.04	5.0
Lead	P^{32}	2.9	80.0	4.8
	Ba^{140}	3.9	2.0	4.2
	I^{131}	3.6	3.0	4.1
Polished Stainless Steel Type #347	P^{32}	3.7	0.3	3.2
	Ba^{140}	7.3	0.04	5.7
	I^{131}	8.7	0.007	6.5
Unpolished Stainless Steel Type #316	P^{32}	2.5	0.8	2.5
	Ba^{140}	4.0	0.8	3.9
	I^{131}	6.1	0.06	4.9
Bonded Stainless Steel Type #302	P^{32}	3.9	0.6	3.7
	Ba^{140}	5.9	0.4	5.5
	I^{131}	4.9	0.05	3.6
Micro Rold Stainless Steel Type #302	P^{32}	4.2	0.5	3.9
	Ba^{140}	6.2	0.2	5.5
	I^{131}	4.9	0.1	3.9

to the fact that the cleaning reagents attack the surface. In this, and similar cases, the quantity of activity removed per step does not necessarily level off as fast as it does when the surface is not attacked. However, in the later stages of reagent cleaning, the fraction of the activity removed is not at all commensurate with the degree to which the surface is eroded.

A comparison of Table V with the data of Table VI indicates that any of these materials can be used routinely up to the mc level of activity although more vigorous treatment would be required to keep lead cleaned, and difficulty would be encountered when P^{32} is used in conjunction with stainless steel. If the laboratory is subjected to a heavy work load (high frequency of operation) at this level, the time spent in maintenance and cleaning would probably be excessive and auxiliary protective measures such as those recommended as standard radiochemical practice would be mandatory if the laboratory is to be used efficiently.

If these materials are used with higher activity levels, one must be prepared to finish each cleaning operation by a procedure which removes some of the surface layers. A possible exception may be the use of Type 316 or 347 stainless steel with I^{131}. The very good figures obtained with the polished stainless steel are due largely to the mirror finish which, unfortunately, tends to become tarnished by laboratory fumes. Therefore, the net benefit hardly justifies the additional cost.

Materials which are cheaper, more easily fabricated and more easily cleaned must be found if the cost of satisfactory facilities for "hot" laboratories is to be reduced. Such a surface should be smooth, nonporous and, although chemically resistant, it should be possible to remove practically monomolecular layers without pitting or roughening the cleaned

area. In view of the fact that good reagent decontamination depends primarily on preventing surface reaction, water repellent properties should be high on the list of requirements for a decontaminable surface.

SUMMARY

It has been shown that the exchange of a radionuclide between surface and solution is an inherently slow process. Decontamination of a surface depends largely on the removal of radionuclides which are not attached to, or are loosely held by the surface. Simple tests which permit comparisons between surfaces, cleaning reagents and contaminating conditions have been developed. A few conclusions regarding the suitability of glass, stainless steel, and lead for radiochemical laboratory surfaces have been drawn.

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FOOTNOTES

(1) Based on work done in the Biology Division, Oak Ridge National Laboratory under Contract No. W-7405-eng-26 for the Atomic Energy Commission.

(2) Present address, Naval Radiological Defense Laboratory, San Francisco, California.

(3) Isotopes Division, Atomic Energy Commission, Oak Ridge, Tennessee.

(4) "Contamination" results from the attachment of a radionuclide to a solid surface; "decontamination" involves its subsequent removal. By common usage, a material is considered a "decontaminable material" when it can be cleaned by liquid solvents without undue deterioration (5).

(5) No isotopic carrier added deliberately during the production. The total solids were of the general order of 1 mg/25 ml.

(6) The ratio $\left(\frac{\text{Activity on the surface before cleaning}}{\text{Activity on the surface after cleaning}}\right)$ is called the Decontamination Factor, D.F.

(7) Frosted glass was used for this particular experiment so that less active P^{32} solutions could be used. The frosted glass provides a better adsorptive surface than smooth glass.

(8) It is sufficient for our purposes to consider the radioelement to be in exchange equilibrium with the surface when the activity adsorbed maintains a constant value for 10 hours with the plaque immersed in the solution. This value was reached at about 20 hours.